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ON

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SEPTEMBER 10-12 1992

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WELCOME TO ECOF'92

Organizing the fourth in this series of European Conferences has been a particular pleasure for us at Bangor. The regular attendees will know that one of the aims of these meetings has always been to improve the interaction between European research groups. Judging from the large number of presentations from groups collaborating across international boundaries the foresight and initiative of the original organizers has been amply justified.

The emergence of techniques such as STM and AFM, Brewster angle microscopy, surface plasmon resonance spectroscopy and fluorescence techniques has significantly improved our understanding of monolayers at the air-water interface and of built-up multilayers. I am sure that the discussions and deliberations at this conference will result in further insights and developments in our field.

Can I take this opportunity to thank all my colleagues in the Institute of Molecular and Biomolecular Electronics who have given freely of their time to ensure the success of this meeting. Also, my thanks go to the following organizations for their support:

- British Telecom plc
- European Office of the United States Army
- ICI plc
- Institute of Physics
- Royal Society of Chemistry
- Science and Engineering Research Council
- Sharp Laboratories of Europe
- Unilever plc

On behalf of the organizing committee can I wish you a very pleasurable and productive time while you are in North Wales.

Martin Taylor, Chairman, Local Organizing Committee

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4TH EUROPEAN CONFERENCE ON ORGANIZED ORGANIC THIN FILMS

PROGRAMME

THURSDAY, 10TH SEPTEMBER

1.30 pm Registration

3.45 pm Opening Remarks

4.00 pm -

SESSION A:

5.40 pm

Structure of monolayers and LB Films

- OA1 *Phase multiplicity and thermal behaviour of fatty acid LB-Multilayers. A systematic X-ray and optical study on the influence of sample preparation and interlayer interactions.* A.Leuthe, D.Ducharme and H.Riegler (Germany/Canada)
- OA2 *Investigation of photoinduced structural changes in monolayers at the air-water interface using Brewster angle microscopy.* R.C.Ahuja, D.Hönig and D.Möbius (Germany)
- OA3 *Structure/Optics relations of 2D cyanine dye crystals.* S.Kirstein, V.Bliznyuk and H.Möhwald (Germany/Ukraine)
- OA4 *The roles of chain and headgroup in determining amphiphilic monolayer phase structure.* I.R.Peterson (Germany)
- OA5 *Correlation between domain shape and structure of phospholipid monolayers.* A.Dietrich and H.Möhwald (Germany)

5.40 pmTea....

6.10 pm -

SESSION A (continued)

7.30pm

- OA6 *Molecular-hydrodynamic description of the kinetics of Langmuir-Blodgett deposition.* J.G.Petrov and P.G.Petrov (Bulgaria)
- OA7 *Imaging domain structures in Langmuir-Blodgett films with atomic force microscopy.* L.F.Chi, H.Fuchs, R.R.Johnston and H.Ringsdorf (Germany)
- OA8 *Faceting of bidimensional crystals in Langmuir monolayers.* C.Flament and F.Gallet (France)
- OA9 *Advantage of the energy-dispersive x-ray reflectivity technique for studying time-dependent processes in Langmuir-Blodgett multilayers.* H.J.Merle, G.Schulte, H.Metzger and U.Pietsch (Germany)

7.45 pm -Buffet Reception....

FRIDAY, 11TH SEPTEMBER

9.05 am -

SESSION B:

10.25 am

Supramolecular Structures

- OB1 *Periodic supramolecular arrangement of three different polyelectrolytes as an example for tailor-made layer-by-layer construction of multilayer film assemblies.* Y.M.Lvov and G.Decher (Germany)
- OB2 *LB-transfer of flow-compressed monolayers of polyelectrolytes.* T.Michel and W.Nitsch (Germany)
- OB3 *From monomolecular films to bulk liquid crystals.* M.Eberhardt and H.Gruler (Germany)
- OB4 *Crystal engineering in two dimensions: Creation of new monolayer single crystals using close-packing principles.* C.J.Eckhardt, P.Dussault, J.Takacs, P.Beak and R.A.Uphaus (USA)

10.25 am Coffee....

10.50 am -

SESSION B: (continued)

12.30pm

- OB5 *Flexoelectricity of lipid and lipid-peptide bilayer membranes. The role of ion channels.* A.G.Petrov and P.N.R.Usherwood (Bulgaria/UK)
- OB6 *The electromechanical properties of interfaces.* T.J.Lewis, J.P.Llewellyn and M.J.van der Sluijs (UK)
- OB7 *Withdrawn*
- OB8 *Structural study of the first two-dimensional polymer.* D.Lefevre, P-A.Albouy and S.Palacin (France)
- OB9 *Preparation of thin metallic layers by means of Langmuir-Blodgett films.* D.Brandl, K.Hege, Ch.Schoppman and H.Voit (Germany)
- OB10 *Y-layers of short chain amphiphiles by thermal evaporation.* Z.Ali-Adib, P.Hodge, R.H.Tredgold and M.F.Woolley (UK)

12.30 pm -

2.00 pm Lunch....

2.00 pm -

4.20 pm Poster Session....

4.20 pm -

SESSION C:

6.00 pm

Molecular Electronics

- OC1 *Langmuir-Blodgett films of fullerenes.* G.Williams, A.J.Moore, M.R.Bryce, A.Hirsh, Y.M.Lvov and M.C.Petty (UK/Germany/Russia)
- OC2 *Further evidence for molecular rectification in M/C₁₆H₃₃- γ Q₃CNQ/M structures.* A.S.Martin and J.R.Sambles (UK)

- OC3 *Defects in conduction LB films.* A.Barraud, J.P. Bourgoin and M.Vandevyver (France)
- OC4 *Photolithographic encapsulation of an integrated electrochemical multielectrode device using thin films.* G.Williams and C.D'Silva (UK)
- OC5 *Electric field control of photo-induced optical anisotropy in molecular chromophore films.* S.P.Palto, L.M.Blinov, G.Grewer and M.Lösche (Russia/Germany)

6.00 pm Tea....

6.30 pm -

SESSION D:

7.10 pm

Non-Linear Optical Properties

- OD1 *Noncentrosymmetric Langmuir-Blodgett films for second harmonic generation.* G.J.Ashwell (UK)
- OD2 *Surface induced orientation of molecules studied by optical second-harmonic generation.* M.Pinnow and G.Marowsky (Germany)

7.15 pm Dinner....

SATURDAY 12TH SEPTEMBER

8.45 am -

SESSION E:

10.45am

Optical Properties and Characterisation

- OE1 *Photoinduced surface potential changes in ferrocene derivative monolayers at the air-water interface.* R.C.Ahuja, T.Kondo, M.Fujihira and D.Möbius (Germany/Japan)
- OE2 *Surface enhanced contrast (SEC) microscopy - a new tool for in situ characterization of ultrathin films of polarisable and hyperpolarisable molecules.* M.Flörsheimer, K.Sutter and P.Günter (Switzerland)
- OE3 *A novel optical technique for Langmuir-Blodgett film analysis.* S.G.Cooke and G.G.Roberts (UK)
- OE4 *Structural investigations of phospholipid LB films with integrated optics.* J.J.Ramsden (Switzerland)
- OE5 *Optical absorption properties of mixed ferrocene derivative Langmuir-Blodgett films.* M.B.Grieve, A.J.Hudson, T.Richardson and C.Honeybourne (UK)
- OE6 *Polarised attenuated total reflection FTIR studies on molecular microstructures in ω -tricosenoic acid Langmuir-Blodgett Films.* Y.P.Song, M.C.Petty and J.Yarwood (UK)

10.45 am Coffee....

11.15 am -
12.55 pm

SESSION F:
Molecular Recognition

- OF1 *The streptavidin/biotin system as a docking matrix: molecular recognition and 2D-crystallization on streptavidin monolayers.* C.H.Erdelen, M.Hoffmann, W.Müller, E.Rey, H.Ringsdorf, P.A.Suci, E.Rump and Zhang Xi (Germany)
- OF2 *Specific binding of streptavidin to self-assembled monolayers on gold: a systematic study.* J.Spinke, M.Liley, F.-J.Schmitt H.J.Guder, L.Angermaier and W.Knoll (Germany/Switzerland/USA/Japan)
- OF3 *Polymerisation of avidin and streptavidin with various bisbiotin ligands.* H.Morgan, H.Fukushima, D.M.Taylor and C.D'Silva (UK)
- OF4 *Interaction of amphiphilic barbituric acid and pyrazolidine-3,5-dione derivatives with trisaminopyrimidin and nucleobases in mono- and LB-multilayers.* R.Ahuja, P.L.Caruso, D.Möbius, W.Paulus, H.Ringsdorf and G.Wildburg (Germany)
- OF5 *Molecular recognition processes characterized at the molecular length scale.* D.Vaknin, K.Kjaer, M.Piepenstock and M.Lösche (USA/Germany/Denmark)

12.55 pm CLOSE OF CONFERENCE

POSTER SESSION

Structure of Monolayers & LB Films

- AP1** *Preparation and characterization of thin fullerene films.* T.R.Schindler, U.Scheunemann, H.-U. ter Meer, W.Hickel and A.Mathy (Germany)
- AP2** *Studies of the flow of condensed Langmuir monolayers.* B.R.Malcolm (UK)
- AP3** *Slow structural rearrangement of a sidechain phthalocyanine polymer at the air-water interface.* C.F.Van Nostrum, M.N.Teerenstra, M.A.C.Devillers, G.T.Jostergetel, A.J.Schouten and R.J.M.Nolte (Netherlands)
- AP4** *Preparation of Langmuir-Blodgett films from an azo-benzene derivative.* B.Stefanov, G.R. Ivanov, J.Petkova, A.G.Petrov and D.Tsankov (Bulgaria)
- AP5** *Withdrawn*
- AP6** *Dependence of the multilayer-water interfacial pK_i on the number of deposited monolayers.* J.G.Petrov and D.Möbius (Bulgaria/Germany)
- AP7** *Interaction free energies of Langmuir-Blodgett multilayers of docosylammonium phosphate.* J.G.Petrov and A.Angelova (Bulgaria)
- AP8** *Interaction of long-chain amine monolayers with polivalent counter-ions from the aqueous subsolution.* A.Angelova and J.G.Petrov (Bulgaria)
- AP9** *The structure of poly(naphthoylene benzimidazole)-stearic acid mono- and multilayers.* V.N.Bliznyuk, I.I.Ponomariov and A.L.Rusanov (Germany)
- AP10** *On the nature of specific interactions and adhesional forces between Langmuir monolayers and various substrate interfaces.* M.Engel and H.Riegler (Germany)
- AP11** *Morphological instabilities and condensation microstructures in Langmuir monolayers at the air/water/substrate three-phase line.* K.Graf, K.Y.Lee and H.Riegler (Germany)
- AP12** *Controlling the structure and morphology of 2-Docosylamino-5-nitropyridine (DCANP) from the microscopical to the AFM scale.* F.Klinkhammer, G.Decher, L.F.Chi and H.Fuchs (Germany)
- AP13** *Langmuir-Blodgett multilayer films of water-soluble amphiphiles deposited from polyelectrolyte containing subphases.* F.Essler, J.-D.Hong and G.Decher (Germany)
- AP14** *LB-Deposition and structure investigation of discotic multiyne mesogens* J.Reiche, D.Janietz, D.Hofmann, H.Lemmetyinen, R.Dietel and L.Brehmer (Germany/Finland)
- AP15** *Corrections of the intensity of x-ray diffraction for Langmuir-Blodgett films.* A.Sabisch, T.Gutberlet, M.Kastowsky and H.Bradaczek (Germany)

- AP16 *Mixed alkanethiol monolayers on gold surfaces: Substrates for Langmuir-Blodgett films deposition.* P.Sanassy, S.D.Evans, D.N.Batchelder and A.Ulman (U.K./USA)
- AP17 *Structural study of L.B. films of a rigid-rod polymer by x-ray diffraction.* P.A.Albouy and N.Schaub (France/Germany)
- AP18 *Stereocomplexation of isotactic and syndiotactic PMMA in a Langmuir monolayer.* R.H.G.Brinkhuis and A.J.Schouten (Netherlands)
- AP19 *The influence of counterions and hydrophobic moieties on the thermostability of LB multilayers.* U.Höhne and H.Möhwald (Germany)
- AP20 *Structural and compositional variations in monolayers before, during and after the LB-transfer as a result of substrate-layer interactions.* K.Spratte and H.Riegler (Germany)
- AP21 *Cis-trans isomerization of azobenzene amphiphiles at the air/water interface.* R.C.Ahuja, J.Maack, P.L.Caruso, M.Matsumoto, and D.Möbius (Germany/Japan)
- AP22 *Characterisation of Langmuir-Blodgett films with the atomic force microscope.* J.P.K.Peltonen, H.Pingsheng and J.B.Rosenholm (Finland/China)
- AP23 *Supramolecular Structure with C_{60}/C_{70} in Mono- and Multilayers.* J.Effing, U.Jonas, H.Ringsdorf, F.Diederich, C.Thilgen, and D.Weinstein (Germany/USA)
- AP24 *Monolayer behaviour and LB-transfer of poly-(4-vinylpyridinium) type polyelectrolytes.* J.Wagner, T.Michel and W.Nitsch (Germany)

Biological

- BP1 *Tethered and mobile supported bilayers as model membranes.* C.H.Erdelen, L.Jullien, H.Ringsdorf, R.Merkel and E.Sackmann (Germany)
- BP2 *The incorporation of the channel forming proteins into Langmuir Blodgett films of phosphatidic acid.* P.J.Lukes, M.C.Petty and J.Yarwood (UK)
- BP3 *Monofilm and X-ray diffraction investigations of the amphiphilic constituents of the cytoplasmic membrane of staphylococcus aureus.* Th.Gutberlet and H.Bradaczek (Germany)
- BP4 *Monolayers of LPS extracted from rough mutant bacteria.* H.Morgan and D.M.Taylor (UK)
- BP5 *Withdrawn*
- BP6 *Monolayer characterisation and surface enhanced Raman spectroscopy of photosystem II reaction centres.* R.Picorol, S.Yu.Zeitsev, G.D.Chumanov, M.Seibert, T.M. Cotton and R.A.Uphaus (Spain/Russia/USA)
- BP7 *Domain structure and molecular conformation in films from fluorescently-labelled phospholipids.* G.R.Ivanov and R.Brasseur (Bulgaria/Belgium)

- BP8 Preparation of Langmuir-Blodgett films from fluorescently labelled phospholipids. G.R.Ivanov and J.Petkova (Bulgaria)
- BP9 Gating behaviour of porin channels in Montal-Mueller bilayer membranes: C.M.Jones, D.M.Taylor, H.Morgan, J.Lonsdale and R.Southgate (UK)
- BP10 A modular trough for Langmuir-Blodgett deposition and Montal-Mueller bilayer studies. L.S.Miller, A.L.Rhoden and A.J.Cranston (UK)
- BP11 Ionic selectivity of valinomycin and crown ethers in monolayers. S.Yu. Zaitsev and V. Zubov (Russia)

Self Assembly

- CP1 Self-assembled monolayers of non-alkane thiols: The influence of intermolecular backbone interactions. M.Liley, J.Spinke H.-J.Guder, L.Angermaier and W.Knoll (Germany/Japan)
- CP2 Self-assembled organic films on gold. H.Keller and J.Dembowski (Germany)
- CP3 Sandwiched protein layers: Layer-by-layer deposited multilayer assemblies of streptavidin and biotinylated poly-L-lysine. M.Lovack, J. Hong and G.Decher (Germany)
- CP4 Self-assembled multilayers of ω -mercaptoalkanoic acids: Effect of incorporating bulky polar groups. T.Freeman, S.D.Evans and A.Ulman (UK/USA)
- CP5 Self-assembled monolayers of host molecules on gold. E.U.Thoden Van Velzen, J.F.J.Engbersen and D.N.Reinhoudt (Netherlands)

Supramolecular Structures

- DP1 Molecular ordering in Langmuir-Blodgett films from discotic liquid-crystalline compounds. V.V.Tsukruk, J.H.Wendorff, O.Karthauss, and H.Ringsdorf (Germany/Ukraine)
- DP2 Alternate layer LB Films containing polysiloxane monolayers. W.H.A.Majid, T.Richardson, S.Holder and D.Lacey (UK)
- DP3 Electropolymerisation of substituted furans and thiophenes leading to conducting films. D.J.Lax, W.R.Reed, G.Singh and J.Yates (UK)
- DP4 Structure, morphology and phase transitions in freely-suspended, transferred freely-suspended and LB-films of liquid-crystalline *n*-alkyl-4'-*n*-alkoxybiphenyl-4-carboxylates. J.Reibel, U.Sohling, G.Decher, R.M.Overney, E.Meyer, J.Frommer and H.J.Günterodt (Germany)
- DP5 Layer-by-layer deposited supramolecular film assemblies of anionic and cationic polyelectrolytes: An x-ray study of the thermal behaviour and the effects of added salt. J.Schmitt and G.Decher (Germany)
- DP6 Spreading behaviour of norbornene monomers and polymers. A.Laschewsky, W.Schultz-Hanke and M.Seitz (Germany)

- DP7 *Kinetics of polymerization of the acrylic and diacetylene lipid-like monomers in monolayers.* S.Yu.Zaitsev, E.V.Plyasova, E.N.Grishina and V.P.Zubov (Russia)

Sensors

- EP1 *Vapour detection using a polypyrrole film coated AT-crystal.* C.D'Silva and R.Pennington (UK)
- EP2 *Biosensors fabricated with L-B films of derivatized pyrrole.* B.Popov and D.Farmakovsky (Russia)
- EP3 *Highly specific SPR immunosensor based on streptavidin/biotin technology.* H.Morgan and D.M.Taylor (UK)
- EP4 *Interactions involving hydroxytryptophan-, dihydroxynaphthalene-lipids, DMPA and cyclobis (paraquat-p-phenylene) at the air-water interface.* R.C.Ahuja, P.L.Caruso, D.Möbius, D.Philp, J.Preece, H.Ringsdorf, J.F.Stoddart and G.Wildburg (Germany/UK)

Molecular Electronics

- FP1 *Rubbed LB-films used as coupling-layers for surface stabilized ferroelectric liquid crystal displays.* T.Rupp, M.Eberhardt and H.Gruler (Germany)
- FP2 *Quantum chemical investigations of the photoactive charge transfer supermolecules, supramolecules and design of the molecular devices.* A.Tamulis and L.Bazhan (Lithuania/Russia)
- FP3 *Characterisation of LB films of mono- and di-valent salts of didodecyldimethylammonium-metal (dmit)₂.* E.Barlow, S.K.Gupta, D.M.Taylor, A.E.Underhill and C.E.Wainwright (UK)
- FP4 *Reflection of the surface acoustic waves from the edge of resonance layer.* J.Alekna and E.Lioliene (Lithuania)

Non-linear Optics

- GP1 *Noncentrosymmetric Langmuir-Blodgett-multilayers for second harmonic generation.* W.Hickel, U.Falk, D.Lupo, and U.Scheunemann (Germany)
- GP2 *Second harmonic generation from LB mono- and multilayers of poly(isocyanide)s.* M.N.Teerestra, R.D.Klap, A.J.Schouten, M.A.C.Devillers and R.J.M.Nolte (Netherlands)
- GP3 *Phase-matched frequency-doubling in Langmuir-Blodgett film waveguides* M.Küpfer, M.Flörsheimer, Ch.Bosshard and P.Günter (Switzerland)
- GP4 *Aminonitrostilbene carboxylic acid LB films for electrooptics.* J.P.Cresswell, M.C.Petty, N.M.Ratcliffe, D.Adevimpe and M.Shepherd (UK)
- GP5 *Chemical and photochemical properties of Gedye merocyanine Langmuir-Blodgett films.* J.P.Hoarau, S.Isz, J.P.Morand and J.C.Mialocq (France)
- GP6 *Langmuir-Blodgett films of polysiloxanes functionalised for non-linear optical applications.* L.S.Miller, D.J.Walton, P.J.W.Stone and R.S.Sethi (UK)

GP7 *Thick polymeric Langmuir-Blodgett films for efficient second harmonic generation.* Z.Ali-Adib, P.Hodge, T.A.King and D.West (UK)

Optical Properties & Characterization

HP1 *Photoinduced charge transfer in rhodamine B/anthracene mixed LB multilayers.* E.Vuorimaa, M.Ikonen and H.Lemmetyinen (Finland)

HP2 *Determination of lateral diffusion coefficients in air-water monolayers by fluorescence quenching measurements.* F.Caruso, F.Grieser, A.Murphy, P.Thistlethwaite, R.Urquhart, M.Almgren and E.Wistus (Australia/Sweden)

HP3 *Optical surface heterogeneities measured by Ellipsometry: Fatty acid and lipid Langmuir monolayers at the air/water interface.* M.Paudler and H.Riegler (Germany)

HP4 *On the correlation between viscoelastic and structural properties of Langmuir monolayers at the air/water interface. Ellipsometric and surface light scattering studies.* J.Ruths, J.Li and H.Riegler (Germany)

HP5 *On the study of the morphology of the Langmuir-Blodgett films of long chain dynoic acid using FT-IR and raman imaging techniques.* P.Sanassy and D.N.Batchelder (UK)

HP6 *Preparation and optical characterisation of porphyrin derivatives as Langmuir and LB films.* A.J.Hudson, T.Richardson G.G.Roberts, R.A.W.Johnstone and A.Sobral (UK)

LAUDA

Film Balance

The LAUDA film balance is an equipment for the investigation of monolayers of polar substances (proteins, lipids, polymers, diaphragm investigation, etc.) on subphase liquids according to the method of Langmuir.

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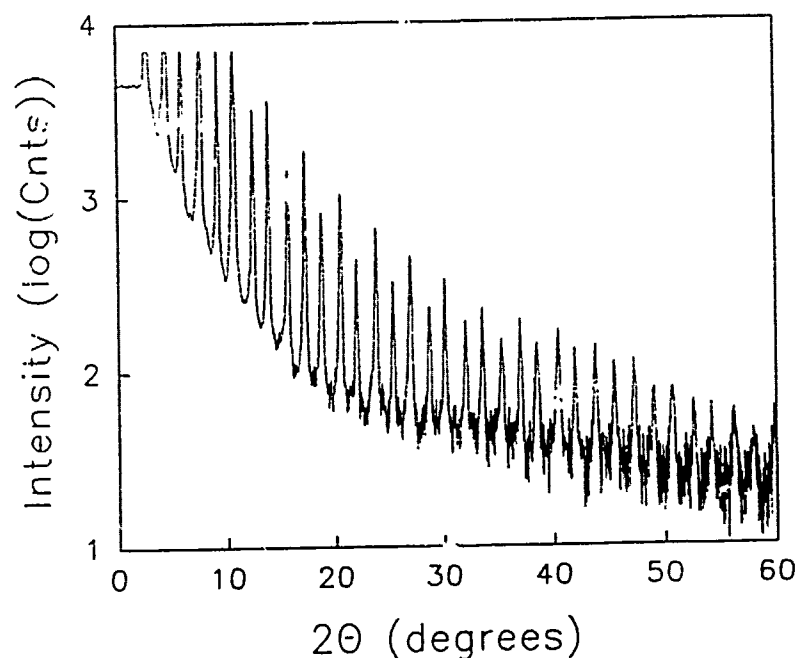
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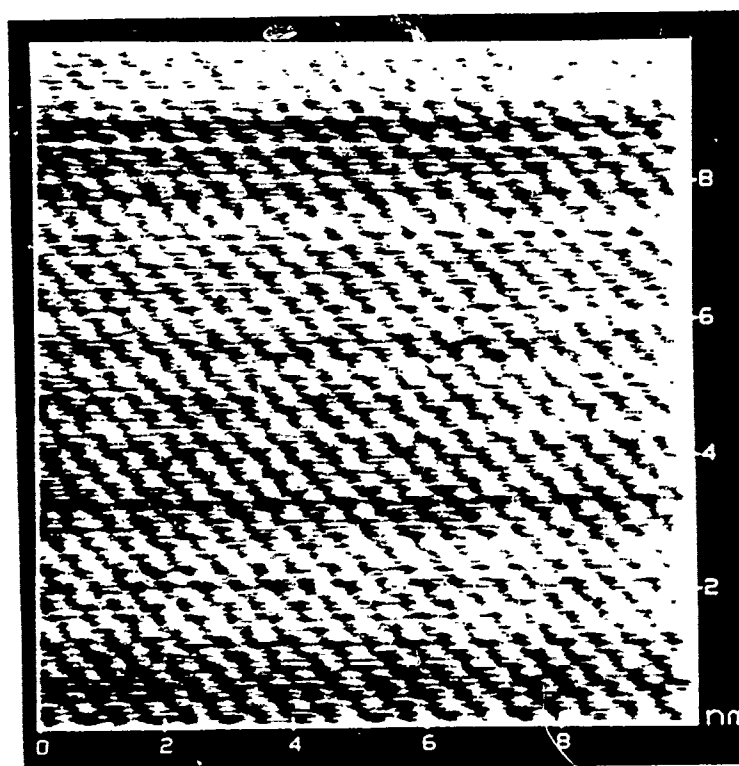
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Towards perfect Langmuir-Blodgett films...



X-ray diffraction peaks of 50 layer Cd-arachidate LB film deposited on a Nima trough. Diffraction peaks were visible up to 60° incidence, implying a single crystal structure over several mm. Work was performed at the Department of Physics, Queen's University, Kingston, Ontario by David Amm and David Johnson.

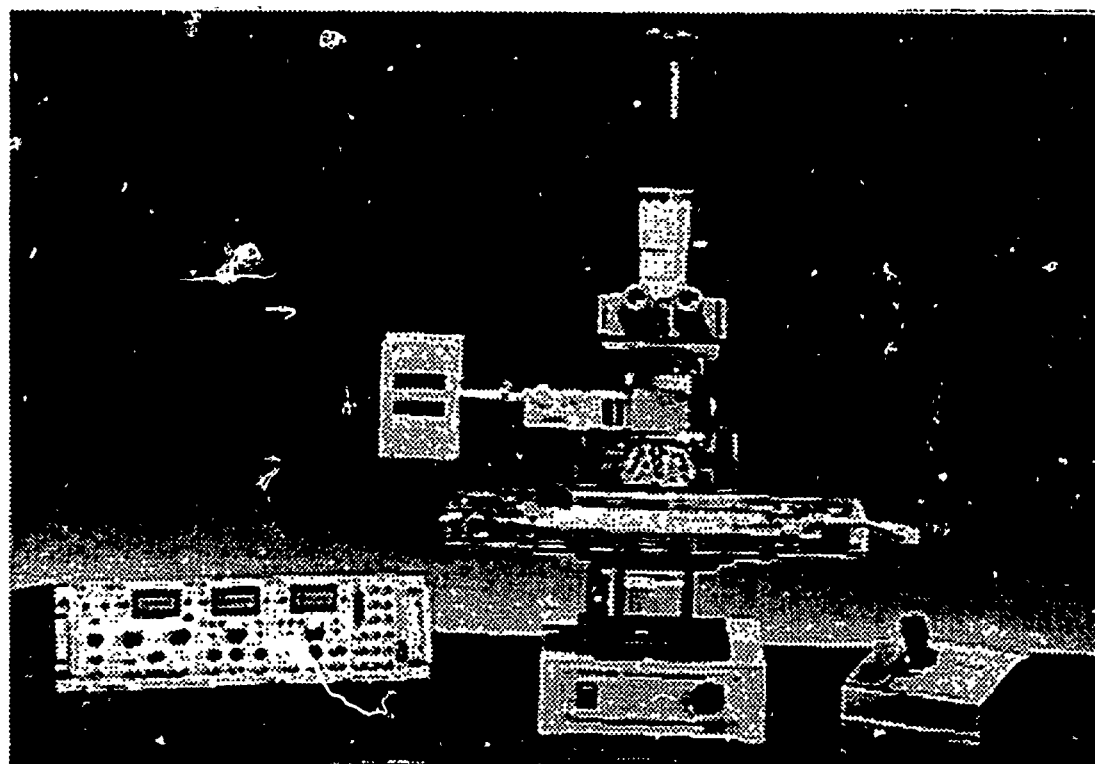
Atomic force micrograph of a 4 layer Cd arachidate LB film deposited with a Nima trough. The picture shows an almost perfect hexagonal close packed order over 100nm^2 . The work was performed at the Department of Nuclear Engineering, University of California, at Santa Barbara by DK Schwartz, J Garnaes, R Viswanathan & JAN Zasadzinski. See 'Scanning' 14, 1992, p11-3.



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SESSION A:
STRUCTURE OF MONOLAYERS AND LB FILMS

Phase Multiplicity and Thermal Behaviour of Fatty Acid LB Multilayers. A Systematic X-ray and Optical Study on the Influence of Sample Preparation and Interlayer Interactions

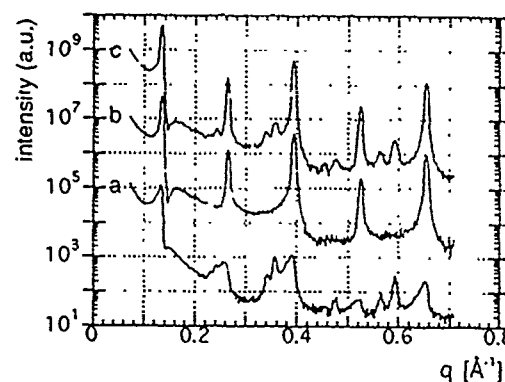
Axel Leuthe, Daniel Ducharme[†], and Hans Riegler

Institut für Physikalische Chemie, Universität Mainz, Welter-Weg 11, 6500 Mainz

[†]*Permanent address: Centre de Recherche en Photobiophysique a Trois-Rivieres, Trois-Rivieres, Quebec, Canada G9A 5H7*

The structure and thermal behaviour of behenic (docosanoic) acid multilayers deposited onto silanized silicon surfaces with the Langmuir-Blodgett technique were investigated by x-ray diffraction and polarized light microscopy. Various multilayer samples were prepared from the L2, L2', and CS monolayer phase. Irrespective of the different phases of the precursor monolayers on water, all deposited multilayers showed similar Bragg peak triplets from three coexisting phases with 48.3 Å, 52.8 Å, and 55.8 Å bilayer thickness, corresponding to tilt angles of $\approx 36^\circ$, $\approx 28^\circ$, and $\approx 21^\circ$, respectively. The samples differed only in the relative peak intensities. Several factors, e.g. substrate surface preparation, deposition conditions (speed, etc.), and the phase of the precursor flow influence the relative amounts of the coexisting three phases. The observed layer spacings exactly match the large repeat units of the three behenic acid bulk phases. None of the obtained multilayer phases equaled the structures of the precursor monolayers from which the samples were prepared. Once heated to $\approx 65^\circ\text{C}$, all multilayer samples annealed irreversibly into the maximum tilted phase with 48.3 Å bilayer spacing; the Bragg peaks of the 52.8 Å and 55.8 Å bilayer spacings disappeared. Regardless of the annealing, the multilayers remained a film of uniform thickness as proven by pronounced Kiessig fringes. Reflection polarized microscopy revealed a grainy morphology (grains \approx micron diameter) with locally varying brightnesses (birefringence) for the unannealed samples. In case of the annealed samples, domains with diameters of

several tens of microns and uniform birefringence were observed. Additional layers deposited on top of annealed (monophasic) multilayer templates were again triphasic and qualitatively not different from those directly deposited onto silanized silicon wafers. Based on the experimental results models of the multilayer architectures are



Diffractograms of the various preparational stages of a mixed unannealed/annealed behenic acid multilayer sample prepared from the L2' phase:

a) unannealed multilayer (25 Y-type bilayers)

b) same multilayer at room temperature after thermal treatment at 65°C for several minutes

c) same annealed multilayer topped with 10 additional unannealed bilayers (also prepared from the L2' phase).

The triplets of plot c) clearly indicate the coexistence of the three phases in the sample.

presented. It is suggested that the layers consist of stacks of epitaxially grown domains of uniform bilayer spacings. Arachidic and stearic acid multilayers showed triphasic structures and annealing properties analogous to behenic acid.

Investigation of photoinduced structural changes in monolayers at the air/water interface using Brewster angle microscopy

Ramesh C. Ahuja, Dirk Hönig and Dietmar Möbius
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The reflectivity at the interface between two non-absorbing and isotropic media with refractive indices n_1 and n_2 depends on the polarization of the incident light beam and the angle of incidence α . In the case of p-polarized light and an ideal interface, the reflected light intensity is zero at the Brewster angle [$\tan \alpha = n_2/n_1$]. Based on this principle, we have developed a highly sensitive technique which allows unperturbed microscopic observation of various physico-chemical processes at the interfaces. The Brewster reflectivity of a monolayer at the air/water interface depends on the lipid chain length, lipid surface density, lipid-lipid interactions in the monolayer and lipid head group/subphase interactions. As the probing light does not have to be absorbed by the monolayer, it is possible to investigate light sensitive molecules. In this communication, we concentrate our attention on various photoinduced processes such as cis-trans isomerization of azobenzene amphiphilic monolayers, photobleaching of hemicyanine monolayers and the photopolymerization of amphiphilic diacetylene monolayers at the air/water interface. It is shown that the Brewster angle reflectometry and microscopy is a sensitive technique for the investigation of these processes at interfaces.

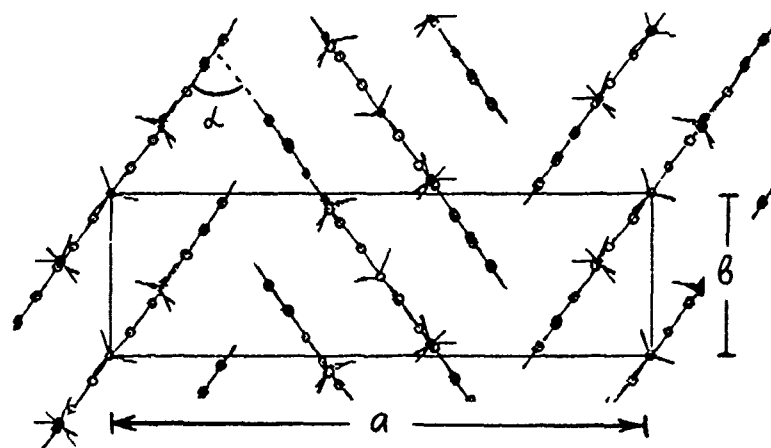
Structure / Optics Relations of 2D Cyanine Dye Crystals

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Optical properties (absorption and fluorescence spectra) with their connection to the structure of mixed cyanine dye crystals were investigated. The latter were prepared by adsorption of water-soluble dyes to oppositely charged surface of a lipid monolayer during compression at the air-water interface / 1 /. Emission spectra and the morphology of such systems were observed in situ during the formation of crystals at the water surface by means of a Langmuir trough integrated into a fluorescence microscope and with the help of multichannel optical spectral analyzer (OSMA) connected to it. To investigate the optical absorption and the structure of the dye crystals thus obtained they were transferred to a glass substrate covered with formvar or to the thin formvar films on top of copper grids (for the electron diffraction (ED) measurements) respectively. Unit cell parameters of twodimensional crystals were determined from the ED patterns. The values of the angle between the chromophore long axes in the neighbouring stacks of dye molecules in the crystals were extracted both by absorption spectra decomposition into the two lines of Davidov splitting and by computer simulation of ED patterns (Fourier transformation of the suggested dye molecule packing model - see figure below). The angles thus determined agree.



Structural parameters can be varied by preparing mixed crystal with appropriate composition of slightly different dyes. Thus also the optical properties can be changed while maintaining sharp absorption edges. By this, absorption band edge and emission peak positions can be tuned in the range of ~ 20 nm.

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THE ROLES OF CHAIN AND HEADGROUP IN DETERMINING AMPHIPHILIC MONOLAYER PHASE STRUCTURE

OA4

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It is important to understand how the structure of an LB film arises from the structure of the precursor monolayer on the water surface. The present paper addresses the relationship between the local molecular packings on the water surface, immediately after deposition, then sandwiched between many others in a multilayer assembly. In the Steitz plot of Figure 1, the two lowest-order in-plane d-spacings from a wide range of aliphatic amphiphiles in a range of different environments^{1,2} are plotted against one another. Hence for a given local packing and area per molecule, the parameters are completely defined,

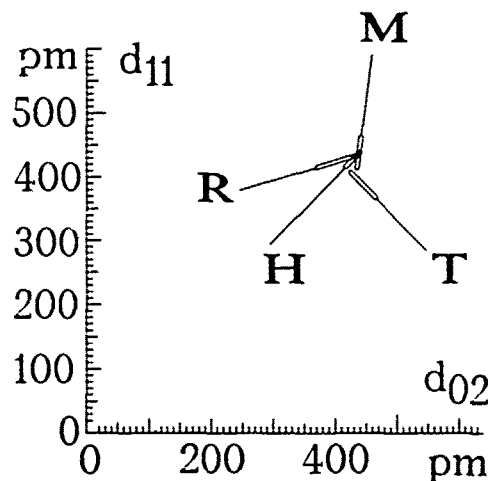


Figure 1. Steitz plot of d-spacings for aliphatic-chain lamellae. The sausage width contains 70% of the observed points. The labels are the Kitaigorodskii symbols for the probable local chain packing^{1,2}.

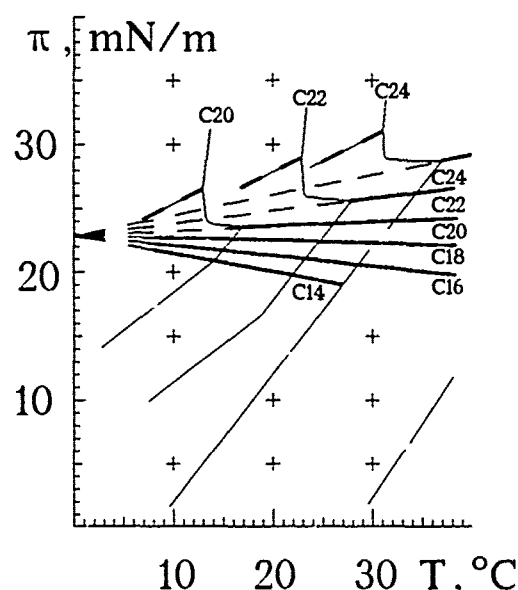


Figure 2. The π -T phase diagrams for the C14-C24 fatty acids.

irrespective of the headgroup and its interaction with the environment.

Assuming that this constancy reflects the monolayer thermodynamics, it is shown that the surface pressure of a given second-order phase transition should vary linearly with chain length at a given temperature. The agreement of this prediction with experiment is shown in Figure 2 for the L₂-LS transition.

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Correlation Between Domain Shape and Structure of Phospholipid Monolayers

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During the last ten years the techniques of x-ray diffraction, electron microscopy and especially epifluorescence microscopy have been well established and are very useful methods for observing coexisting phases of monomolecular films and interfaces. Studying the monolayer behaviour of coexisting phospholipid molecules via fluorescence microscopy at the air/water interface yields a variety of domain shapes that depend sensitively on the competition between domain boundary energy and electrostatic repulsion between molecules within and between domains. The investigation of branched chain phospholipids offers the possibility to manipulate the interactions of headgroup repulsions since the area per headgroup of these molecules is larger than needed for non-branched systems.

Here we report on x-ray and electron diffraction studies with monolayers of branched chain phospholipids in comparison with fluorescence microscopy results at the air/water interface. The systems with a third branched chain are two isomeric phosphatidylcholines which differ in the position of the branched chain at the glycerol backbone and yield two different domain shapes observed in the LE/LC phase coexistence range: one compound exhibits a mostly hexagonal shape, since the other shows a smooth domain boundary. X-ray diffraction studies on the water along the pressure/area isotherms reveal identical packing densities but deviations from the hexagonal symmetry of the lattice formed by aliphatic tails, depending on the branch position. For a system with four branched chains the hexagonal symmetry is obtained.

By transferring these molecules from the phase coexistence regime onto a solid support prepared for transmission electron microscopy we have investigated that for three different polymer substrates (Formvar, Formvar/SiO_x, PMMA) the domain shapes are conserved in case of Formvar and extremely distorted for PMMA substrates.

But the related data obtained from electron diffraction do not show any significant difference in the microstructure spacings between different substrates although there is a condensing effect on the monolayer due to the transfer from the liquid to the solid interface.

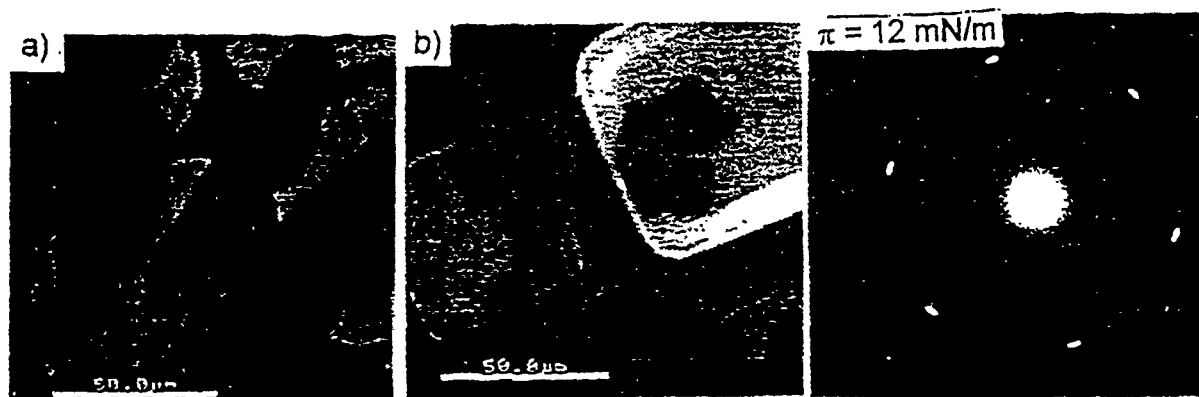


Figure 1: Typical picture of the transferred phospholipid domains from the phase coexistence region onto different polymer substrates that cover electron microscopy grids (a) 1-(2C₁₄-16:O)-2H-PC on PMMA, (b) 2-(2C₁₄-16:O)-2H-PC on Formvar and the obtained diffraction spots.

MOLECULAR - HYDRODYNAMIC DESCRIPTION OF THE KINETICS OF LANGMUIR - BLODGETT DEPOSITION

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Abstract

The transfer of a monolayer from a liquid/gas interface onto a solid substrate takes place at the three-phase contact line where the solid/liquid, gas/liquid and solid/gas interfaces meet each other. Thus the kinetics of the Langmuir-Blodgett deposition is determined by the velocity of the contact line, V . The existing theoretical expressions relate this velocity to the dynamic contact angles, θ , on the basis of molecular (Blake, 1967; Blake and Haynes, 1968) or hydrodynamic (Voinov, 1976; Cox, 1986) considerations. A semi-quantitative combination of the two approaches has been proposed earlier (Petrov and Radoev, 1981). This investigation presents a complete analytical expression for the theoretical θ/V -relationship taking into account both the molecular-kinetic and hydrodynamic mechanisms in the case of stopped tangential motion at the liquid/gas interface due to the presence of insoluble monolayer on it. The application of the equation obtained to our previous and other literature θ/V -data for different LB-systems shows which microscopic and macroscopic physical parameters might determine the kinetics of the monolayer deposition.

Imaging Domain Structures in Langmuir-Blodgett Films with Atomic Force Microscopy

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Atomic force microscopy (AFM) investigations on phase separated Langmuir-Blodgett (LB) films deposited on polymeric layers are reported. The experiments demonstrate the ability of the method to image details of the domain structures of stearic acid (C_{18}) which cannot be recorded by fluorescence microscopy (Fig.1). On a scale of $30 \times 30 \mu m^2$ up to $100 \times 100 \mu m^2$ the AFM images resemble those observed with fluorescence microscope (Fig.2). By applying the force modulation technique it was found that the elastic properties of the crystalline domains are comparable to those found for the grains within the liquid-analogous phase. In addition, AFM allows to investigate the influence of the transfer conditions on the shape of the domains. Further, the effects of the presence of trace amounts of fluorescence dye mixed in C_{18} films on the domain structure are discussed.

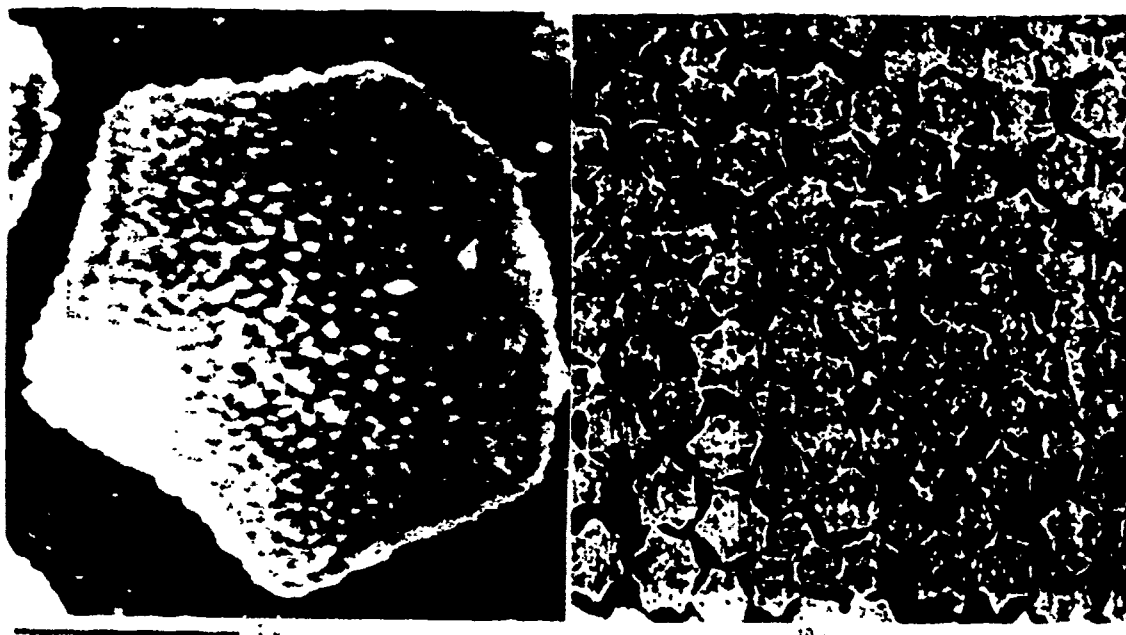


Fig.1

Fig.2

Faceting of bidimensional crystals in Langmuir monolayers

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We are interested in the morphology of ordered domains in Langmuir monolayers. At high molecular density these bidimensional systems may have positional order, as shown by X-rays or electrons diffraction experiments. Otherwise these domains can be directly observed by epifluorescence microscopy experiments. The visualization is possible by adjonction of a fluorescence probe or by using only a pure fluorescence molecule in the film. It has been shown that some of them are faceted.

At equilibrium state there are two kinds of generic shape : with faceted or with rough boundary lines. Our theoretical approach has consisted in modelizing the bidimensional solid phase by a homogeneous assembly of particles which interact through an isotropic pair potential : $V_n(R) = -C_n/R^n$ ($n > 0$) where R is the distance between two particles. We have shown, in the large domain size limit, that the boundary energy is proportional to the boundary length only for the case $n > 3$. For $n \leq 3$ a line tension cannot be defined and thus we must reconsider the general result, that the boundary of a bidimensional crystal, where a line tension exist, is rough at any temperature. To characterize the boundary state we have considered the competition between the thermal fluctuations which tend to delocalize the boundary and a periodic pinning potential, which tends to localise it along a straight line (a reticular line of the bidimensional lattice). The boundary state is determined by the averaged value of the pinning potential over all the boundary configurations. A calculation at the lowest order shows that for $n > 2$ the boundary is rough, and faceted for $n < 2$, at any temperature. For $n = 2$ the boundary state depends on the temperature : at low temperature the boundary is faceted whereas it is rough at high temperature. A roughening transition may happened at a finite temperature T_R given by $2k_B T_R = b^2 \sigma^2 C_2$, where b is the periodicity between reticular lines, σ the two dimensional density of particles, and C_2 the potential amplitude.

The roughening transition could be observed in Langmuir monolayers because in these bidimensional systems amphiphilic molecules carry either an electrical charge or an electrical dipole moment, and so interact through a long range potential (i.e. $n \leq 3$). In particular we discussed the cases $n = 1$ i.e. interaction between two finite charges (with screening effect), $n = 2$ i.e. interaction between a monopole and a dipole, and between two dipoles in a strictly bidimensional geometry (where electric field is confined).

Advantage of the energy-dispersive x-ray reflectivity technique for studying time-dependent processes in Langmuir-Blodgett multilayers

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Introduction

Recently it has been shown that Langmuir-Blodgett (LB)-films of Cd palmitate exhibit apparently a coexistence region of two different phases near the melting point of the ordered structure [1]. With increasing temperature the volume fraction of the LB phase decreased whereas that of the new phase increased. This measurement was carried out by angular resolved x-ray scattering, which is usually employed for the determination of the layer spacing [e.g. 2,3].

For the study of dynamic processes the energy-dispersive technique (EDT) is advantageous because the scattering angle is fixed during the measurement and all energies are detected simultaneously resulting in a shorter detection time for the whole spectrum [4]. This method was previously used to determine the kinetic behaviour of the thermal induced structural phase transition in Cd stearate multilayers [5].

Results

The time dependence of the x-ray reflectivity of various Cd soap multilayers was recorded at fixed temperatures ΔT below the melting point T_S . T_S is defined as the temperature where the characteristic layer pattern of the LB film vanishes completely. During the heating of a virgin sample to $T = T_S - \Delta T$ we find a decrease of the lattice spacing between 2 - 5 %. Additionally the total intensity of the multilayer Bragg peaks decreases continuously with time. The decrease of the integrated peak intensities as a func-

tion of time follows a pure exponential law in the case of Cd palmitate. LB films of Cd stearate and Cd arachidate show a non exponential behaviour.

After about 30 to 45 minutes new peaks appeared which correspond to a new phase. Their angular positions indicate a lattice spacing larger than a monolayer but smaller than a bilayer. The melting point of the new phase is much larger than T_S .

We interpret the new phase as a hexagonal packed columnar arrangement of the Cd soap molecules similar to that known in bulk material [6].

The phase transition from the LB phase to the new one may be explained by the interplay of at least two simultaneous factors: firstly the order-disorder properties of the original structure, and secondly the increased mobility of molecules at defects (grain boundaries, etc.). The latter enables the molecules to form a state not showing SAXS peaks. Within this state the nucleation of the new phase takes place.

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SESSION B:
SUPERMOLECULAR STRUCTURES

PERIODIC SUPRAMOLECULAR ARRANGEMENT OF THREE DIFFERENT POLYELECTROLYTES AS AN EXAMPLE FOR TAILOR-MADE LAYER-BY-LAYER CONSTRUCTION OF MULTILAYER FILM ASSEMBLIES

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INTRODUCTION

During the last three years we have developed a new technique which allows to construct ultrathin multilayer assemblies by consecutive adsorption of anionic and cationic polyelectrolytes out of aqueous solution [1-4]. The principle of this layer-by-layer adsorption is schematically depicted in Fig. 1. Our method allows the fabrication of functional multilayer films (e. g. films containing protein layers; poster CP3) that can be deposited on surfaces with any given topology. They show excellent thermal stability and the total film thickness can be adjusted to within a few Ångströms (poster DP5).

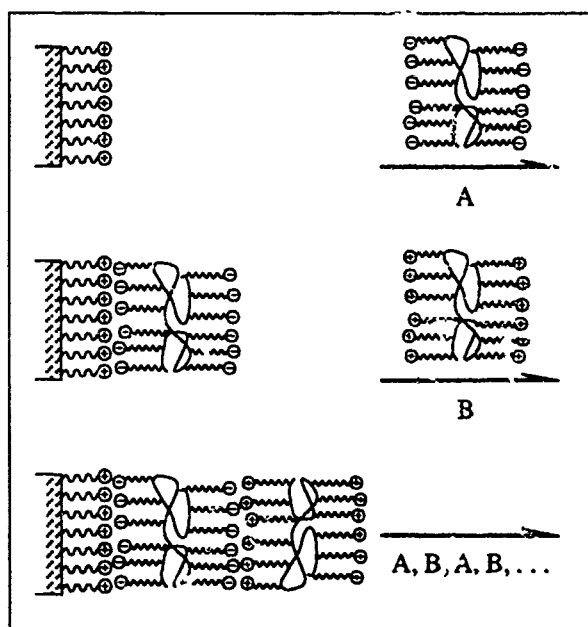


Figure 1: Side-view schematic depicting the consecutive adsorption of polyelectrolytes (polymer structures are highly idealized). A positively charged substrate is immersed in the solution containing the anionic polyelectrolyte and a monolayer of the polyanion is adsorbed (step A). After rinsing, the substrate is immersed in the solution containing the polycation, again, a monolayer of the cationic polyelectrolyte is adsorbed, thereby restoring the original surface charge (step B). Cyclic repetition of both steps (A, B, A, B, ...) yields alternating multilayer assemblies of both polymers.

Here we report on the construction of multicomponent films consisting of more than two polyelectrolytes, i.e. films with predetermined alternation of three or more different compounds in a ABAB...CDCD... or ABCDABCD... fashion.

RESULTS

The polyelectrolytes were: polystyrenesulfonate deposited from solutions containing 0.5m MnCl (PSS/Mn), 2.0m CsCl (PSS/Cs) and 2.0m NaCl (PSS/Na), polyvinyl-sulfate (PVS) and polyallylamine deposited from solutions containing no salt (PAH) and 2.0m NaBr (PAH/Na). Fig. 2 shows the growth of a 10 layer (PVS-PAH) film on top of a 12 layer (PSS/Cs-PAH/Na) film as monitored by X-ray reflectivity. Both films exhibit a linear, self-consistent growth, but the layer directly at the interface slightly deviates from the normal value.

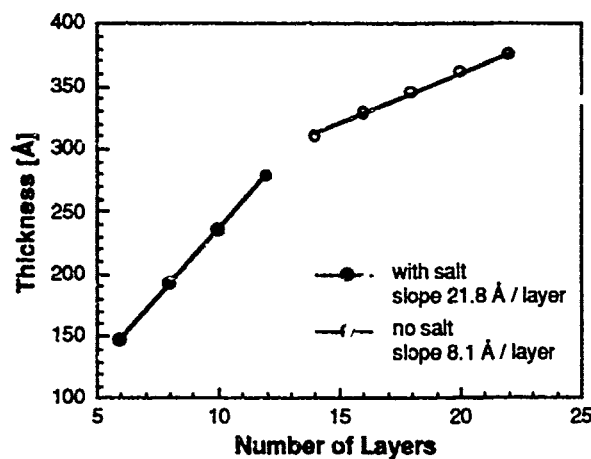


Figure 2: Growth of a 10 layer (PVS-PAH) film on top of a 12 layer (PSS/Mn-PAH/Na) film

This influence of the previous layer on the following one is even better observed when different layer pairs are strictly alternated. For multicomponent supramolecular assemblies composed of alternating layer pairs of (PSS/Mn-PAH/Na) and (PVS-PAH) or (PSS/Cs-PAH) and (PSS/Na-PAH) the film thickness was always more than the sum of the respective pure films. We tentatively propose that the diffusion of electrolyte ions into the next layer is responsible for the observed effects.

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LB-transfer of flow-compressed monolayers of polyelectrolytes

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The interaction between moving liquid subphases and adsorbed or spread monolayers on the surface of these subphases can be used to compress the layers to states which can be compared with the classical method via the Langmuir-trough. The driving force for this compression is the local shear stress of the flowing liquid, acting directly beneath the monolayer covered surface. Using a simple flat canal and adjusting it that the height of the flowing subphase is the same across the length of the canal, one can measure a perfect linear increase of film pressure along the compressed monolayer. At all points of the compressed monolayer the same force acts and the same force balance between the local gradient in film pressure and the local shear stress is maintained (1).

This method was applied to soluble and insoluble polyelectrolyte systems. As soluble polyelectrolytes poly-allylamine hydrochloride (PAAH) and poly-4-vinylpyridinium (P4VP) chloride were used and alkyl derivatives of poly-4-vinylpyridinium with high degree of quaternization as insoluble polyelectrolytes.

Only in the presence of soluble surface active counterions (i. e. dodecylsulfonate and -sulfate, perfluorooctanoate (PFOA)) stable and significant stagnation layers of PAAH and P4VP can be generated. Very low concentrations of polymer (e. g. 1 mg/dm³) and amphiphile (e. g. 1 10⁻⁵M) can be used. The monolayers are spontaneously formed by adsorption. For sufficiently low concentrations of polymer and amphiphile the same results are obtained for the adsorbed layers as for spread monolayers. As a contrast extremely high collapsed, but stable states of these systems can be obtained, depending on the length of the canal and/or on the flow rate. The remarkable effect is, that these collapsed states can be transferred to solid substrates with perfect reproducibility per each dipping cycle. Microweighing with quartz crystal resonators indicate, that the mass deposited during LB-transfer are indeed multiples of the monolayer equivalent. Up to forty-fold equivalents of the monolayer mass can be transferred with exact the same increments during ten dipping cycles at minimum. But for these systems the transferred collapsed states are turbid and not homogeneous.

Using an octyl derivative of P4VP as an insoluble representative — spread on PFOA — triple layers of quat-P4VP/PFOA complex can be generated and transferred with Y-type behaviour, these layers have the same properties as if they were built up from monolayer deposition (characterized by quartz microweighing and ellipsometry).

These results demonstrate that flow compression of monolayers is a suitable tool to prepare monolayers (even from water soluble compounds) for LB-transfer. Moreover, even for practical reasons this method may have the advantage, that stable "monolayer stacks" (collapse) can be generated very easily and directly. The large areas for compression necessary in the classical trough-method are avoided. Additionally it may be an advantage — especially for polymer layers — that the "driving force" for compression acts on every point of the whole layer and not only on the surrounding or from one side (barrier) of the monolayer.

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FROM MONOMOLEKULAR FILMS TO BULK LIQUID CRYSTALS

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Investigating thermotropic liquid crystals on the Langmuir trough, a substance called HOBACPC¹ showed a completely new behaviour in its π -A diagram². The diagram showed several coexistence regions with constant pressures, separated by collapse-points at areas in the relation 1 : 1/2 : 1/3 etc., suggesting that smectic layers have been built. It could be shown, that the transition from $n \rightarrow n+1$ layers is an equilibrium transition in a thermodynamic sense. The transition is found to be of first order at temperatures below 30° and of second order above. Looking at the transition-pressures, the first layer is shown to be of lower symmetry than the subsequent ones. Measurements of the surface contact potential and the displacement current showed, that only the first layer has a polar orientation. But even the change from a totally polar to an apolar layer structure is not enough to explain the differences between the first layer and the other ones. Therefore the subphase (water) must have a large contribution to the interfacial free energy of the system.

To get more information about the dynamics of multilayer formation the optical retardation of the film was investigated under compression. The results showed that there is a change from a smectic C to a smectic A phase always before a collapse point is reached.

¹hexyloxy benzylidene-amino-chloro-c. propylcinnamate

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CRYSTAL ENGINEERING IN TWO DIMENSIONS: Creation of New Monolayer Single Crystals using Close-Packing Principles

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Over the last decade, many areas of research and technology have focussed attention on Langmuir-Blodgett (LB) films. They serve as useful model systems for biology and physics or function as modifiable systems for materials and engineering applications. Detailed control of film structure promises much in understanding their formation and extending their function. Their study has been limited because of nearly complete emphasis on fatty acid amphiphiles which have yielded distorted hexagonal planar lattices exhibiting very short range order. These nets have in some cases shown dependence on the structure of the solid subphase. In any event, only one or two of the seventeen possible planar space groups have been observed for LB films.

Close-packing principle arguments show that proper control of the amphiphile cross-section, chirality and rigidity permits formulation of amphiphile molecular structures which will lead to the formation of other planar lattices. Atom-atom potential calculations verify the more qualitative arguments and have lead us to synthesize new amphiphiles. This deliberate design and synthesis has made it possible to create heretofore unobserved two-dimensional crystals. The new amphiphiles have cross-sectional geometries which are elliptical, triangular and rectangular.

Because the cross-sectional geometry of fatty acid amphiphiles (all trans configuration) is not circular, an amphiphile of more triangular geometry has been synthesized. Because there are five hexagonal nets, it is important to have amphiphiles which may pack into this general type of lattice. Further, the molecule is designed to be quite rigid and possesses a unique interlocking geometry intended to yield both strength and order. The atomic force microscopy (AFM) of the monolayer on mica shows it to be, within error, hexagonal and it displays orientational coherence lengths on the order of 200 Å. The surface isotherm co-area and that of the AFM measurement are in agreement.

The racemate of the quite rigid elliptical amphiphile has a surface isotherm which indicates three solid phases. AFM study of the monolayer of the most stable phase exhibits a, twinned, strongly oblique packing (group $p1$) not previously observed. By application of rigorous space group symmetry arguments it can be shown that the twins are pure enantiomers thus demonstrating spontaneous resolution in two dimensions. This conclusion is supported by further AFM study of other phases and lattice potential calculations.

The racemate of the rectangular amphiphile displays another previously unobserved two dimensional packing into a rectangular net ($p2gg$). Investigation of this monolayer throughout the scanning limits of the AFM show few defects over the entire film. This order is consistent with an orientational coherence length of one micron.

This work suggests an effective approach to the chemical design of planar lattices.

FLEXOELECTRICITY OF LIPID AND LIPID-PEPTIDE BILAYER MEMBRANES.
THE ROLE OF ION CHANNELS

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Flexoelectric (curvature-electric) effects in model and native membranes containing either ion pores or ion channels were studied in order to clarify the relationship of flexoelectricity to transmembrane ion transport. Model membrane patches containing ion pores induced by some blue-green algal toxins, microcystin-LR and nodularin (oligopeptides), as well as locust muscle membrane patches containing potassium channels were studied. A combination of patch-clamp, oscillating pressure and lock-in techniques was employed.

A correspondence was established between the opening and closing of these membrane pathways and the flexoelectric a.c. current responses of the membrane patches, selectively recorded at the frequency of the periodic curvature variation of the membrane patch. In some cases amplification factors as high as 1000 were registered. Additionally, registration of the second harmonic of the membrane currents recorded under transmembrane voltage difference provided a measure of membrane curvature amplitudes, thus making it possible to determine the membrane flexoelectric coefficient. Values obtained for this coefficient in both artificial and natural membranes correspond more closely to those expected from the molecular theory of flexoelectricity than the results from previous studies of ours.

The present study also showed that flexoelectricity could be an effective driving force for ion transport through membrane pores and channels. Thus, an attractive guest-host system (lipid bilayer containing ion channels) was proposed. It could be applied as a mechanical sensor or a molecular switch in the molecular electronics.

This study was supported by UK SERC and by Bulgarian National Fund "Scientific Studies" (Project F19).

THE ELECTROMECHANICAL PROPERTIES OF INTERFACES

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Models to interpret electrical phenomena occurring at interfaces between a metal electrode and a dielectric or an electrolyte are well-established and invariably involve the electrical double-layer of the interface. It is not always appreciated however, that much of the early theoretical work to develop these models was based on thermodynamic arguments developed particularly by Gibbs' and on an electro-mechanical rather than a purely electrical view of the interface. According to the Gibbs' adsorption equation, change in the potential difference across an interface will change the interfacial energy and the likely consequence will be a mechanical distortion.

We report measurements to demonstrate this effect for certain metal-liquid and metal-solid interfaces using an interferometric technique to detect cyclic mechanical displacements induced by alternating voltages applied to the interfaces. We also show that steady bias voltages can alter the displacement in a controlled way.

The implications of these measurements for the behaviour of organic thin films on metal surfaces will be discussed.

Structural study of the first two-dimensional polymer

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The building up of a true two-dimensional polymer is reported. The polymer is built up via a solid-state polycondensation which occurs between tetrafunctionalized semi-amphiphilic porphyrins preorganized as a regular paving of the plane by the Langmuir-Blodgett technique. The precursor LB film, together with the polymerized one are extensively studied. Hence, the orientation of the macrocyclic rings before and after the polycondensation is derived from linear dichroism, ESR and X-ray measurements. The polycondensation itself is followed by infrared and Raman spectroscopy. Evidences are given for the formation of covalent links between adjacent porphyrins within each monolayer. Transmission X-ray experiments indicate the emergence of a new crystalline phase in the plane of the monolayer after the two-dimensional polycondensation. The solubility behavior of the precursor and polymerized LB films are consistent with the polycondensation process. This two-dimensional polymer exhibits outstanding mechanical properties since holes up to 0,01 mm² in area can be bridged by only one monolayer. This strenghtening of the lateral cohesion of the film, when compared with classical LB films, is consistent with the two-dimensional character of the polycondensation process. The semi-amphiphilic character of the polymerized film allows finally the complete removal of the aliphatic chains from the polymerized LB film leading to a strong ultrathin and chain-free polymerized film..

Preparation of thin metallic layers by means of Langmuir-Blodgett films

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Physikalisches Institut der Universität Erlangen-Nürnberg

Heating of LB-Films consisting of fatty-acid-salts up to 300°C causes desorption of the fatty acids, whilst the metal ions remain on the substrate surface. These ions form thin metal-oxid-layers with a surface density of roughly 10^{14} ions per cm^2 . The surface density can be adjusted by a controlled process. Both the LB-films and the metal-oxid-layers are characterized by following methods:

- 1) Time-of-flight-mass-spectrometry
- 2) RBS
- 3) SEM
- 4) Micro Probe

Y-Layers of Short Chain Amphiphiles by Thermal Evaporation

by

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Well ordered layers of amphiphilic compounds, some of them too short to deposit by the LB technique, have been formed by thermal evaporation *in vacuo* and characterised by X-ray diffraction, optical microscopy and FTIR spectroscopy. Perfluorodecanoic acid, perfluorododecanoic acid and four azobenzene derivatives, two of which are terminated by alcohol groups and two by methyl ester groups, all formed good quality Y-layers if deposited on cooled substrates. In the case of the acids it was possible to use the technique of Barraud *et al.*¹ to diffuse silver into the head to head regions of the films and to detect the resultant change in the X-ray diffraction pattern. The tilt angles deduced from the X-ray measurements and the FTIR measurements agreed well. The two perfluorinated acids are too short to deposit by the LB technique. The azo compounds however, could also be deposited by the LB technique and gave an identical structure to that obtained by thermal evaporation. All four azo materials were initially homotropic but changed on heating to a structure involving a large tilt and consisting of individual domains having strong birefringent properties. This behaviour agrees with that previously reported by us^{2,3} for the two alcohols when they were deposited by the LB techniques.

We have also studied a number of materials terminated by an amide group. Here the behaviour is particularly interesting. Depending on the substrate temperature it is possible to form either a Y structure or a structure in which the d-spacing corresponds approximately to one molecular length. We have given particular attention to N-methylstearanamide [$\text{CH}_3(\text{CH}_2)_{16}\text{CONHMe}$]. Evaporation onto a substrate at -50°C leads to good Y-layers with a d-spacing of 4.37 nm (compared with a molecular length of 2.7 nm). Evaporation onto a substrate at 20°C leads to a structure having a d-spacing of 2.65 nm but, if stored at room temperature, this structure rearranges to give Y-layers over a period of about 2 weeks. LB deposition of this material gives a mixed structure which eventually turns into the Y-form.

We have also studied 4-heptyl, 4-hexyl and 4-pentyl benzoic acids which, immediately after deposition give good inter-digitated Y-layers which were characterised by the techniques listed above. These materials tended to recrystallise over a period of a few days. However, diffusion of silver or cadmium ions into the heptyl benzoic acid stabilised the layer structure.

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SESSION C:
MOLECULAR ELECTRONICS

LANGMUIR-BLODGETT FILMS OF FULLERENES

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Abstract

Multilayer deposition of C_{60} , C_{70} and tertiary butyl C_{60} ($C_{60}H$ T-Bu) has been achieved by the Langmuir-Blodgett (LB) technique. LB deposition of the pure fullerenes and the substituted $C_{60}H$ T-Bu was successful on a variety of substrates including glass, fused quartz and single crystal silicon.

LB films of pure C_{60} could be built-up (Z-type deposition) on solid substrates (1), however, the resultant films were of poor quality. Much improved quality films were achieved by mixing the C_{60} with arachidic acid (AA) in the molar ratio 1:4.2. Preliminary low angle X-ray diffraction results, from a stepped thickness film on single crystal silicon, will be presented for these structures.

A floating film of C_{70} was formed with a surface area per molecule of $\approx 176\text{\AA}^2$ (2), suggesting a film thickness of 1 molecule, with the major axis of the C_{70} ellipsoid lying parallel to the subphase. Unfortunately successful LB film transfer was not possible from this floating film. However, Z-type multilayer deposition was performed from a more concentrated spreading solution (0.54gl^{-1}), with a deposition ratio of 0.7 ± 0.1 . Ellipsometric data indicated the condensed film thickness to be $\approx 95\text{\AA}$ per layer.

A film spread from a $1.8 \times 10^{-4}\text{M}$ solution of $C_{60}H$ T-Bu formed a condensed film with a surface area per molecule of 88\AA^2 at 25 mNm^{-1} , a multilayer film could be built-up from a more concentrated spreading solution ($4.8 \times 10^{-4}\text{M}$) on the subphase and subsequent ellipsometric results suggested a layer thickness of $\approx 55\text{\AA}$ (3). High quality LB films were produced with deposition ratios of 1.00 ± 0.05 , up to film thicknesses of 2000\AA . DC conductivity measurements were measured perpendicular to the molecular plane via a planar Al base electrode and a top Al electrode. The I-V characteristics were Ohmic and a room temperature dc conductivity of $1.9 \times 10^{-12}\text{Scm}^{-1}$ was established.

References

- 1 G. Williams, C. Pearson, M.R. Bryce and M.C. Petty, Thin Solid Films **209**, (1992) 150-152
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Further Evidence for Molecular Rectification in $M|C_{16}H_{33}-\gamma Q3CNQ|M$ Structures

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In previously published results [1] [2] we have demonstrated the rectifying electrical characteristics of $M|LB|M$ junctions constructed from mono- & multilayers of $C_{16}H_{33}-\gamma Q3CNQ$. Recent review articles [3] [4] described this work as possibly the first observations of molecular rectification, with the reservation that the I/V asymmetry may be due to experimental construction. In order to address this possibility, junctions have been fabricated incorporating a form of the molecule in which the zwitterionic nature of the headgroup has been suppressed [5]; whilst sharing some of the unaltered molecule's characteristics, the strikingly large forward bias current passage is no longer evident. Furthermore, in $Ag|22TA|C_{16}H_{33}-\gamma Q3CNQ|22TA|Mg$ junctions, (where 22TA indicates an interposed LB film of ω -tricosenoic acid) large I/V curve asymmetries are again observed (Figure 1), despite the fact that the electrodes are now separated from the $C_{16}H_{33}-\gamma Q3CNQ$ zwitterions by the insulating fatty acid films. These asymmetries exhibit the same functional variations as those of the original junctions, implying that the electrical behaviour is not due to Schottky contacts or electrode/ $C_{16}H_{33}-\gamma Q3CNQ$ interactions. It is thus concluded that the observed electrical rectification is solely due to the intrinsic properties of the $C_{16}H_{33}-\gamma Q3CNQ$ molecule, and that molecular rectification has been observed in a solid state device.

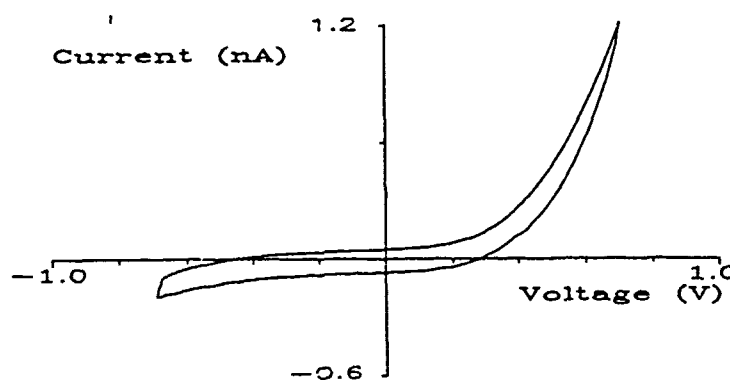


Figure 1: I/V curve for a $Ag|22TA|C_{16}H_{33}-\gamma Q3CNQ|22TA|Mg$ junction in which all the LB layers were of bilayer thickness.

- [1] Geddes NJ et al *Appl. Phys. Lett.* 56 (1990) 1916
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DEFECTS IN CONDUCTING LB FILMS

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Two series of puzzling observations are to be noted concerning conducting molecular LB films :

- 1) the better the quality of the LB film, the poorer their conduction, and conversely ;
- 2) in TCNQ salts series, unexpectedly, it is the most conjugated cations, which should favor conduction by smoothing the lattice potentials, which give rise to the worst conductors ;
- 3) no metal-like conduction (and a fortiori super-conduction) has been obtained in proved lamellar LB films of long chain compounds to date even when non LB parent compounds exhibit a noteworthy metallic conduction ;
- 4) d.c. conductivity decreases as the number of superimposed LB layers is decreased, going to zero for a single conducting plane ;
- 5) conducting Langmuir-Blodgetttable mixed valence compounds are conducting when spread in the form of a single layer at the surface of a glycerol subphase, while they are insulating when transferred from a water subphase
- 6) the d.c. conductivity is always much lower then the microwave and IR one.

In this paper these unanswered questions will be discussed in the light of the large experience now accumulated on molecular Langmuir-Blodgett conductors. Phenomena 1,2,3 involve the intrinsic structure of LB conducting films; phenomena 4,5,6 involve extrinsic structural effects.

Intrinsic defects involve the coexistence of two lattice periods in conducting LB films, that of the conductive stack and that of the aliphatic system. These two periods have no reason to be equal, giving thus rise to structural distortions.

Extrinsic defects result from impurity segregation and cracks generation in the course of film fabrication or chemical film processing (doping for instance).

At the light of these defect generation mechanisms two strategies are considered regarding the improvement of conduction in LB films : homodoping and annealing.^{1,2} In particular, the homodoping strategy allow the fabrication of a conducting single bi-layer and even single layer.

¹ J.P. Bourgoïn, A. Ruau-del-Teixier, M. Vandevyver, M. Roulliay, A. Barraud, M. Lequan, R.M. Lequan, *Makromol Chem. Makromol symp.* **46** (1991) 163.
² S. V. Ayrapetians, T. S. Berzina, S. A. Shikin, V. I. Troitsky, *Thin Solid Films* **210,211** (1992) 261

Photolithographic Encapsulation of an Integrated Electrochemical Multielectrode Device using Thin Films

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The development of multielectrode electrochemical and potentiometric sensors has been inhibited by the lack of availability of suitable waterproof encapsulants. The function of the encapsulant is two fold : (a) to isolate the device from short-circuit by the solution, (b) to create an environment (window or well) within which analysis can be undertaken.

To address this problem, we have explored the use of polymer /azide mixtures as a spin coatable encapsulant and have identified surface treatment, spin coating, irradiation and pattern development conditions. SEM studies (see Fig. 1) on photo-patterned thin films indicate that the thickness of spin coated films is dependent on the concentration of the polymer in the mixture, reaching a maximum value of $13\text{ }\mu\text{m}$ at $3.5 \times 10^{-4}\text{ M}$. The minimum line width attainable using these mixtures under direct UV irradiation through a photomask was $\sim 50\text{ }\mu\text{m}$ for a film thickness of $3\text{ }\mu\text{m}$.

Encapsulant effectiveness was assessed by patterning an integrated multielectrode electrochemical device and evaluation with a reversible redox-active species. Ideal electrochemical behaviour was observed as shown in Fig. 2 and the peak current found to be proportional to $(\text{scan rate})^{1/2}$. The availability of encapsulated electrodes has led to the development of a hand-held electrochemically based environmental monitoring unit (EMU) as shown in Fig. 3.

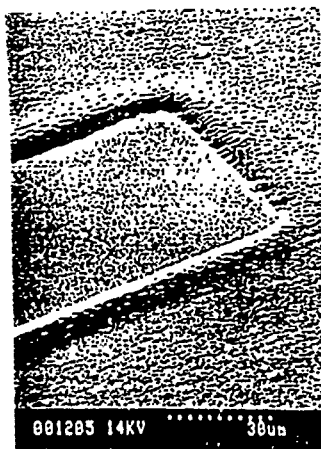


Fig. 1

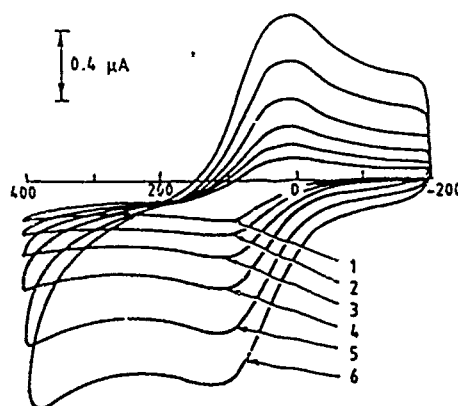


Fig. 2

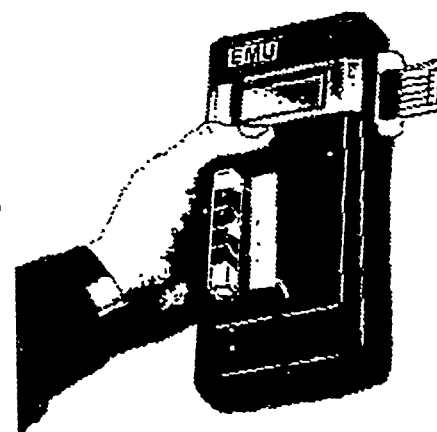


Fig. 3

*Author for correspondence.

ELECTRIC FIELD CONTROL OF PHOTO-INDUCED OPTICAL ANISOTROPY IN MOLECULAR CHROMOPHORE FILMS

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Photo-induced optical anisotropy¹ in molecular organic dye layer systems is thought to be brought about by the local thermal dissipation of the energy of electronically excited states. This enables locally the rotation of chromophores and leads to a statistical reorientation of the molecules.² Thus, the polar order of asymmetrically prepared azo dye LB films decays on illumination into their electronic absorption bands.³

We have utilized the interaction of an external electric field with the ground state dipole moments on the chromophores for the manipulation of this statistical reorientation process.² Thus, the macroscopic polar order of the samples, both in-plane and normal to the interface, may be controlled by the polarized illumination under a static electric field. The initial polar order of samples may be increased or reverted, or polarity may be induced in initially unpolar samples. Due to a threshold behavior of the reorientation with respect to the amplitude of the incident radiation field, the polar order is stable on the time scale of months in dim light at room temperature.

Experimental investigations of the process on the molecular length scale are currently in progress.

The electrostatic interaction energy used to control the reorientation process is much smaller than the thermal energy. This is direct evidence that the reorientation is a collective process. We have modeled the phenomenon using realistic interaction potentials between the molecules and have obtained results which quantitatively comply with the experiments.

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SESSION D:
NON-LINEAR OPTICAL PROPERTIES

NON-CENTROSYMMETRIC LANGMUIR-BLODGETT FILMS FOR SECOND HARMONIC GENERATION

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The phenomenon of second harmonic generation (SHG), whereby a material under illumination doubles the frequency of the incident radiation, requires the structure to be non-centrosymmetric; then for LB films the second harmonic intensity should increase quadratically with the number of layers. This has been realised for film thicknesses to *ca.* 0.7 μm for 4-[4-(dimethylamino)styryl]-1-octadecylpyridinium iodide interleaved with a two-legged spacer molecule, 4,4'-dioctadecyl-3,5,3',5'-tetramethyldipyrromethene hydrobromide. The two-legged amphiphilic molecule was designed specifically as a compatible spacer, the principle being that the hemicyanine tail would penetrate and fasten the interleaving LB layers (a "Molecular Zip"). Micron-thick films with second-order susceptibilities ($\chi_{zz}^{(2)}$) of *ca.* 70 pm/V have been fabricated with a second-harmonic signal which has remained constant throughout a two-year period.

Recently, an improved susceptibility of 500-1500 pm/V has been obtained from monolayer films of the 4-[4-(dimethylamino)styryl]-1-octadecylpyridinium chromophore by replacing the inorganic counterion by octadecylsulphate.¹ The improved signal is probably due to chromophore ordering by way of the alternating amphiphilic cations and amphiphilic anions, the dominant interaction in the aligned films being between the oppositely charged head groups with a weaker van der Waals interaction between the fatty alkyl chains.

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Surface induced orientation of molecules studied by
optical second-harmonic generation

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The alignment of liquid-crystal molecules at a Polyimide surface in liquid crystalline cells is a well known phenomena. We have studied by the optical second-harmonic generation (SHG) the influence of the substrate on the orientation of hemicyanine molecules in thin layers deposited by the wetting- or Langmuir-Blodgett-technique.

At glass and non-treated Polyimide substrate both techniques yield rotational isotropy of the deposited molecules around the surface normal. The tilt angle of the molecules determined for this C_s -symmetry by SHG depends on the concentration of the wetting solution and on the surface pressure during the LBF-deposition.

A rotational anisotropy was detected, when the layers were deposited onto Polyimide-covered glass substrate treated previously by an uniaxial, unidirectional rubbing procedure. The in plane alignment of the molecules is strongly determined by the direction of the rubbing treatment. When the Polyimide is rubbed uniaxially but bidirectionally no anisotropy could be observed, because the resulting bidirectional orientation of molecules is centrosymmetric and therefore not detectable in SH-experiment. The orientational behaviour of the molecules in LBF at high deposition pressure (35 mN/m), the low area per molecule (0.5 nm^2) and the same deposition ratio (0.9) at glass and Polyimide surfaces suggest that not the whole molecule but only the hemicyanine-group in the hydrophilic part of the molecule is aligned in the rubbing direction.

SESSION E:

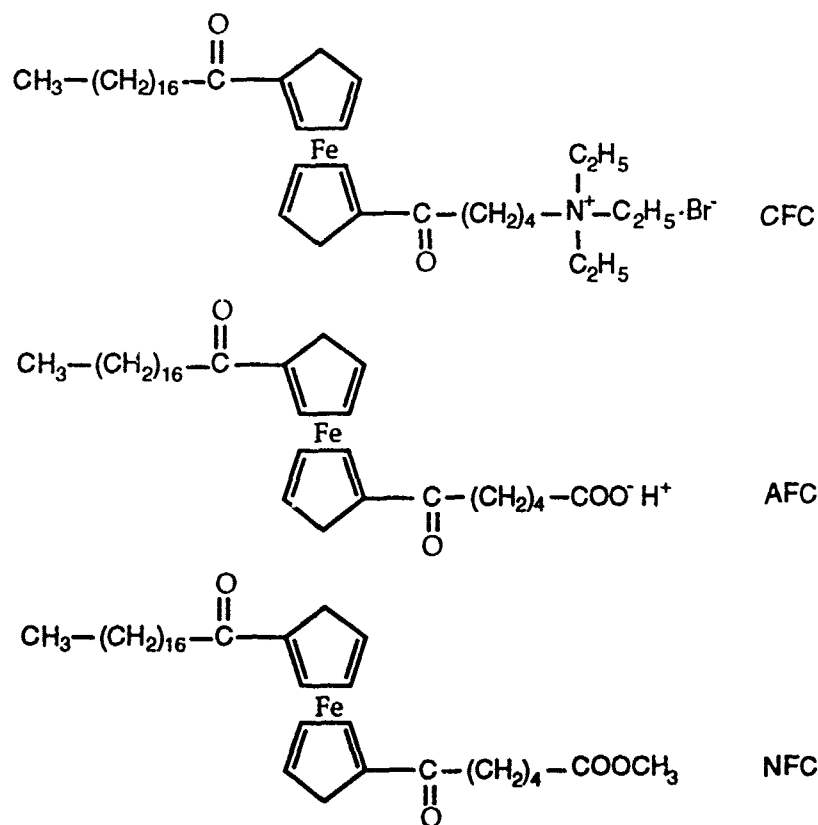
OPTICAL PROPERTIES AND CHARACTERISATION

Photo-induced surface potential changes in ferrocene derivative monolayers at the air/water interface

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Surface potential studies at the air/monolayer/water interface can yield useful information regarding both the structural and electronic properties of the monolayer. We report results of our investigations on monolayers of three amphiphilic ferrocene derivatives, the chemical structures of which are shown below. These three derivatives namely CFC, NFC and AFC have either a cationic $-(C_2H_5)_3N^+$, a nonionic $-COOCH_3$, or an anionic $-COO^-$ head group. The ferrocene moiety is located in the hydrophobic part of the molecule and is separated from the head group by four CH_2 units. Surface pressure-, Surface potential- and Reflection- area isotherms along with UV-VIS reflection spectroscopy measurements were done at the air/water interface. It was found that the surface potential could be reversibly photomodulated by light absorbed by the ferrocene moiety. The magnitude and direction of photoinduced surface potential change was found to be specific to the head group e.g. AFC shows a positive change while CFC shows a negative and NFC does not show any change in the surface potential. These and other results are discussed in terms of molecular models and excited state photophysics of ferrocene moiety.



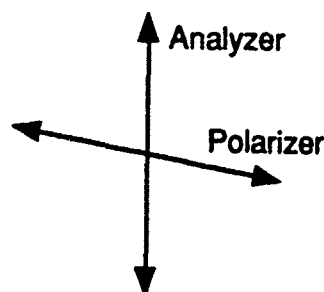
Surface Enhanced Contrast (SEC) Microscopy - a New Tool for in Situ Characterization of Ultrathin Films of Polarizable and Hyperpolarizable Molecules

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A simple microscopical method to image ultrathin films of anisotropically polarizable molecules with outstanding contrast and intensity is described. While in a fluorescence as well as in a Brewster angle microscope the Fresnel reflected light from the thin film support is suppressed, we use a part of this light to enhance the contrast: It is utilized to interfere with the light resonantly scattered from the molecules of the film within the absorption band (Surface Enhanced Contrast - SEC).

The films are observed between linear polarizers which can be freely rotated. The technique reveals information on the orientation of the optical transition moments relative to the polarizer axes and on the range and defects of the orientational order within the films. A monolayer can be observed through the SEC microscope with the naked eye. Staining or decoration of the sample is not required. The lateral resolution amounts to 1 μm .



The photograph shows an area of a monofilm of 2-docosylamino-5-nitropyridine (DCANP) on a water surface spread from chloroform. DCANP is hyperpolarizable and forms LB films with an inplane anisotropy. We prepared multifilms for optical waveguiding with DCANP and demonstrated for the first time phase matched second harmonic light generation (poster GP 3). The structures on the water surface, however, are centric (see SEC image). The anisotropy is induced during the LB film transfer. Decher et al. (Mainz) reported that the anisotropy of the transferred films can be influenced by the selection of the spreading solvent. This coincides with our observations of Langmuir monofilm textures strongly depending on the solvent.

A NOVEL OPTICAL TECHNIQUE FOR LANGMUIR-BLODGETT FILM ANALYSIS

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A new optical technique has been developed, applicable to the study of organic monolayer and multilayer molecular films. Substrates have been studied for which the reflection and transmission of light is very sensitive to the presence of an overlying transparent dielectric film. Relative changes up to 10% may be observed for a Langmuir--Blodgett (LB) bilayer, from normal incidence measurements. Such a measurement is straightforward to perform and to analyse, to obtain quantitative information on film parameters.

The origin of this interference effect has been investigated to determine the optimum substrate. A thin film of metal on a glass substrate can approach this ideal while being compatible with LB deposition. Measurements of the reflectance and transmittance of this substrate as behenic acid bilayers are added have been compared to Fresnel reflectance theory. Film thickness or permittivity information is obtained directly from a simple linear approximation theory, relating the changes observed directly to the film parameters.

Application to film imaging will be presented, in which high contrast has been achieved for bilayer film steps. Other applications to molecular film analysis will be outlined.

ECOF 1992

Structural investigations of phospholipid LB films with integrated optics

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The structure of a thin multilayer structure may be probed by measuring the refractive indices of its constituent layers. The refractive index is directly related to molecular composition via the Lorentz-Lorenz equation.

The electric field distribution of the waveguide modes propagating in an optical waveguide is a standing wave in the waveguiding film and exponentially dying away in the surrounding media. This implies that the phase velocities of the modes depend not only on the optical parameters (geometrical thickness and refractive index) of the material of the, waveguide film itself, but also on those of the environment—the substrate on which the film is supported (usually glass), and the covering medium (e.g. air or water). If a thin film is deposited on the waveguide, its optical parameters may be determined from measurement of the phase velocities of the guided modes.

Phospholipid bilayers were deposited on silicon titanium oxide planar optical waveguides incorporating a grating coupler, using the Langmuir-Blodgett and Langmuir-Schaefer techniques. Phase velocities were determined by scanning the incoupling angle of the waveguide.

The waveguide formed one wall of a cuvette which could be filled with aqueous solutions. Many solutes partition from the aqueous phase into the membrane. Their interaction with the lipid bilayer can be investigated by measuring the kinetics and magnitude of the changes in thickness and refractive index of the membrane. Results from two kinds of substances are reported: small organic molecules (e.g. drugs), and oligopeptides. These two classes behave very differently. The small molecules interact rapidly and reversibly, and frequently have negative partial molar volumes, indicating a contraction of the lipid structure due to the presence of the molecule. The oligopeptides interact irreversibly, with kinetics on a time scale of 1–100 min, and show more complex behaviour.

LANGMUIR-BLODGETT FILMS

M.B.Grieve, A.J.Hudson and T.Richardson

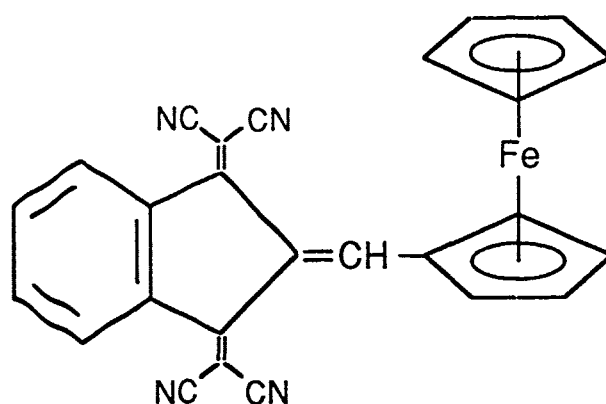
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Langmuir-Blodgett films of a Ferrocene derivative have been prepared and their optical properties investigated systematically. Although lacking the long aliphatic chain characteristic of many LB molecules this Ferrocene compound is stable on the subphase and deposits Z type onto a solid substrate. Due to its dipolar nature and deposition type it is anticipated that this material may exhibit the pyroelectric effect. A study of the pressure-area isotherms for various concentrations of the Ferrocene derivative whilst incorporated into a fatty acid matrix has been undertaken. A series of mixed layer films with the fatty acid were deposited onto a glass substrate using the LB technique. The optical absorption spectra of these films have been studied using linear-dichroism to give an indication of any change in orientation of the chromophore which may occur as the composition is altered. The effect of varying the deposition conditions on the dichroic effect has also been investigated.



Polarised Attenuated Total Reflection FTIR studies on
Molecular Microstructures in ω - *Tricosenoic Acid* Langmuir-Blodgett Films

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Abstract

Thin ω - *Tricosenoic Acid* films with 10, 20, ..., up to 100 monolayers were deposited onto ZnSe and Si ATR crystals by Langmuir-Blodgett deposition techniques. The thicknesses of these films were determined by ellipsometry and Alpha-stepper measurements. Transverse Electric (TE) and Transverse Magnetic (TM) ATR spectra were recorded and the dichroism between the TE and TM absorptions were observed. To interpret the dichroism, we calculated the electric field distributions in the films for both TE and TM modes. From the comparison between the experimental dichroism and the calculation, we were able to obtain detailed information about molecular ordering and orientation in the films.

SESSION F:
MOLECULAR RECOGNITION

The Streptavidin/Biotin System as a Docking Matrix: Molecular Recognition and 2 D-Crystallization on Streptavidin Monolayers

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Due to its high binding constant ($K_a=10^{15} \text{ M}^{-1}$), the biotin/streptavidin system is an ideal tool to investigate the interaction between a membrane incorporated receptor and a protein. Streptavidin is a protein which comprises four identical subunits, each binding one biotin molecule. Injection of streptavidin underneath a monolayer of biotinlipids leads to the formation of large 2 D-crystalline protein domains.[1] Structure investigations revealed, that two of streptavidins four binding sites facing away from the lipid layer are still free for further binding of biotin containing molecules.[2] This suggests the use of the streptavidin layer as a docking matrix for other biotinylated molecules as e.g. proteins and biotinylated linkers, wearing a second ligand function or other functional groups.[3]

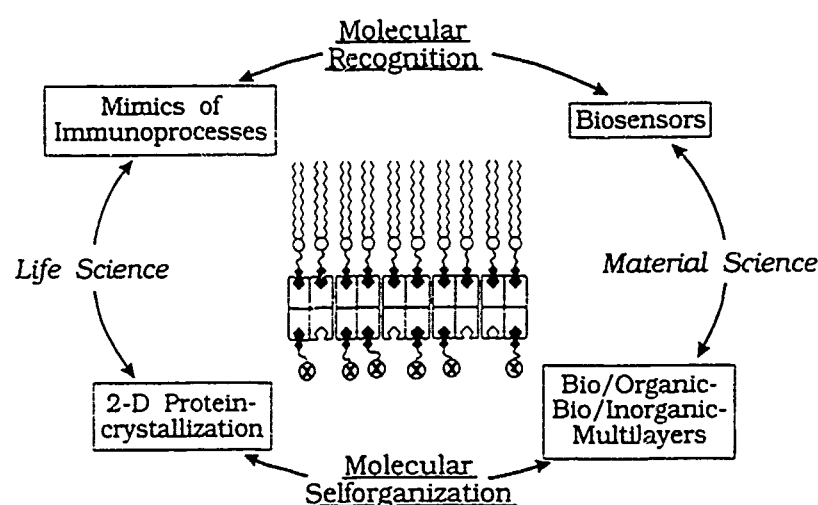


Fig. 1 Tailoring of bioactive surfaces: chances for supramolecular streptavidin assemblies

By the use of a bisbiotin coupler the formation of a second crystalline streptavidin layer under the primary streptavidin matrix could be observed via fluorescence microscopy. Different fluorescent labels allowed to distinguish between the two streptavidin layers.

A second layer of a different protein, concanavalin A (con A), was obtained by the use of a biotin sugar linker. The formation of the con A layer was visualized via fluorescence microscopy. Con A has four sugar binding sites and like in the case of streptavidin the layer of con A still possesses free binding sites facing the subphase. Thus an alternating protein triple layer could be obtained with con A between two streptavidin layers, one facing the biotin lipid layer at the air/water interface, one facing the aqueous subphase.

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Specific binding of streptavidin to self-assembled monolayers on gold: a systematic study

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Self-assembly is an elegant and simple method allowing, in principle, the production of surfaces with well-defined composition and structure. Because of the high degree of control over the chemical and physical properties of the interface which these self-assembled monolayers offer, they have been proposed as model systems for the study of many surface phenomena, including protein adsorption and molecular recognition.

In order to investigate to what extent the promised control and engineering of surface structure can be realised, we have fabricated and studied biotinylated self-assembled monolayers at gold surfaces. The binding of the protein streptavidin to these surfaces was observed using surface plasmon spectroscopy, a relatively simple optical method, which requires no labelling of the protein and has a total internal reflection geometry which allows in situ observation of adsorption processes in solution.

Systematic variation of the self-assembled monolayers (e.g. diluting the biotin groups in the layer; addition of spacer segments) reveals factors important for the efficient specific binding of streptavidin and the suppression of non-specific binding.

The use of desthiobiotinylated self-assembled monolayers and the addition of further protein and peptide layers to the surface leads to a model of a universal immunoassay with reusable substrate.

POLYMERISATION OF AVIDIN AND STREPTAVIDIN
WITH VARIOUS BISBIOTIN LIGANDS

H. Morgan, H. Fukushima, D.M. Taylor and C. D'Silva

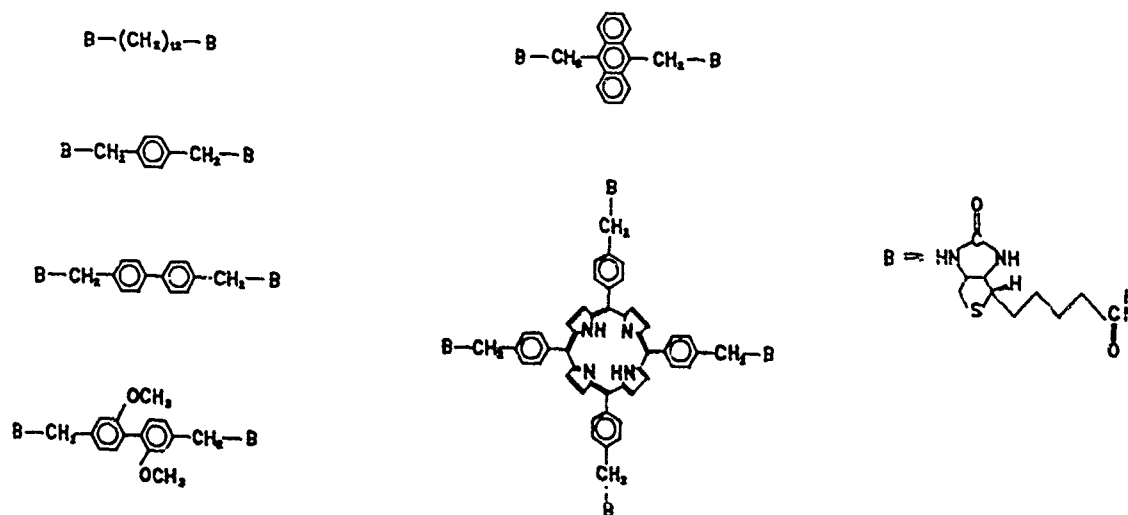
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Abstract

The formation of well ordered arrays of molecules or small molecular aggregates is an important challenge in the field of molecular electronics. In an attempt at forming self organising structures we have made use of the technique of affinity polymerisation whereby essentially irreversible binding occurs between a protein and a complementary ligand. Depending on the number of binding sites on the protein and the structure of the ligand then it should, at least in principle, be possible to assemble a range of different multidimensional networks.

As a first step in the fabrication of such arrays we have utilised the strong affinity of the proteins streptavidin and avidin for the biotin ligand. These proteins have four binding sites for biotin and by using a bifunctional biotin we have been able to make long 1-D polymers and also grow (using directed assembly) protein multilayers on a solid support.

We have now synthesised the range of multifunctional biotin ligands shown below and have investigated their self assembling properties with avidin and streptavidin.

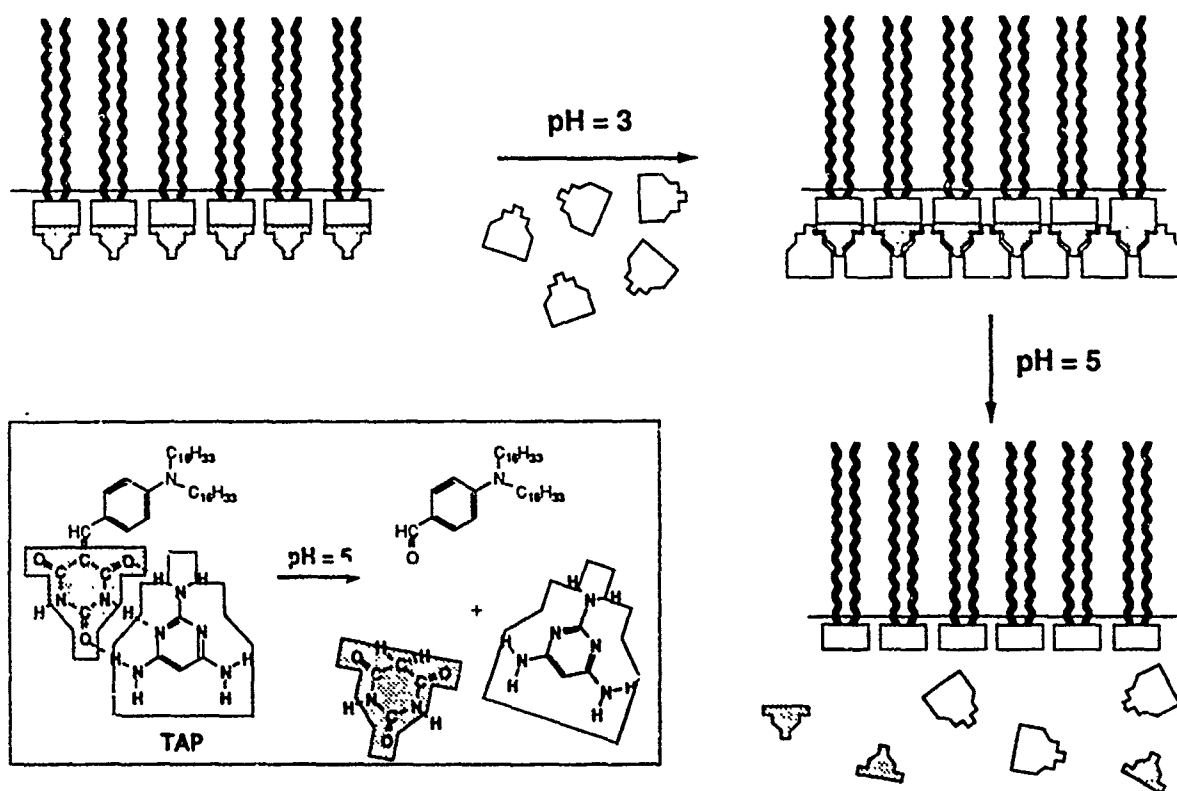


Interaction of amphiphilic Barbituric acid- and
Pyrazolidine-3,5-dione derivatives with Trisaminopyrimidin
and nucleo bases in Mono- and LB-Multilayers

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The interactions of amphiphilic barbituric acid- and pyrazoline-3,5-dione derivatives in monolayers with different subphases containing 10^{-4} mol/l of 2,4,6-trisaminopyrimidine (TAP), melamine, urea and the nucleo bases are described. These interactions were characterized by isotherm measurements, UV-spectroscopy and Brewster-angle microscopy at the gas-water interface and in LB-multilayers.

The aim of these investigations is to see if the H-bonding to TAP in an aqueous subphase is strong enough to justify an expression as molecular recognition. The results obtained indicate that TAP is bound to the barbituric acid at the surface and that the high amine concentration catalyses a basic hydrolysis of the dye at rather low pH (pH=5). This hydrolysis reaction could only be suppressed at a pH of 3. A picture to fit the obtained data is shown below.



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MOLECULAR RECOGNITION PROCESSES CHARACTERIZED AT THE MOLECULAR LENGTH SCALE

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The structural organization of proteins at interfaces and its control are of interest for the comprehension of membrane related biological processes and for the design of protein based sensor devices. We have conducted neutron and x-ray reflectivity measurements on molecular layers at water/air interfaces together with fluorescence microscopic investigations to characterize the molecular organization of phospholipid monolayers^{1,2} and of molecular protein/lipid layer systems.³ While fluorescence microscopy measures the lateral distribution of labeled protein bound to the interface on a μm length scale, from reflectivity measurements the structural organization of the samples normal to the interface is obtained with molecular resolution. From the latter, the macroscopically averaged microscopic lateral organization of the sample may be deduced.

As a model system for a molecular recognition process of a protein at a functionalized interface we have studied the interaction of streptavidin (SA) dissolved in the subphase underneath surface monolayers of biotinylated lipid monolayers. The *in-situ* reflectivity measurements show directly that SA forms monomolecular layers underneath the lipid. The data are interpreted by setting up a geometric model based on the atomic content of each individual layer containing lipid, water, and protein and water, respectively. The geometric parameters are transformed into scattering length density profiles corresponding to different experimental situations: electron density profiles in the case of x-ray reflection and neutron scattering densities in the case of neutron reflectivity measurements from subphases which contain either H_2O or D_2O as the solvent. Thus, one structural model is derived that simultaneously describes *all* reflectivity data sets. The validity of the inherent assumption that the structural organization of the sample does not depend on the isotopic identity of the water is checked with fluorescence microscopic experiments.

We have assessed the water-excluded volume of the protein at the interface and have measured the water content and the average two-dimensional (2D) protein density of the monomolecular film. The latter is in quantitative agreement with 2D electron density maps derived from electron diffraction on similar systems after transfer to Carbon substrates and uranyl staining.⁴ The structural parameters are controlled by the functionalized lipid (lateral density, spacer length between biotin and its lipid anchor) in the surface monolayer.

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P O S T E R S

SESSION A: STRUCTURE OF MONOLAYERS & LB FILMS

Preparation and Characterization of Thin Fullerene Films

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The Langmuir-Blodgett technique was used to prepare fullerene films with and without matrix molecules. The fullerenes were prepared, extracted and purified as described in P. Häussler et. al.*

Fullerenes are non-amphiphilic molecules. They are insoluble in water and form highly compressible, inflexible films at the air-water interface. From the isotherm (20mN/m) the calculated area per molecule is much smaller than theoretically predicted. This effect can only be understood by assuming that a fullerene multilayer is formed at the air-water interface. These pure films could not be transferred to substrates by the vertical dipping technique.

Mixtures of fullerenes with amphiphilic polymers form stable films which can be transferred by Y-type deposition. The amount of fullerenes in mass percentage of the solid film is well defined and can be varied from 0% to 75%. Absorption spectroscopy of mixed films on quartz shows that the deposition is reproducible. The absorbance increases linearly with the number of layers. Compared to uv-vis spectra of fullerenes in solution the spectrum shows a red-shift of 10nm and a slight broadening of the absorption bands. If the number of deposited layers is held constant and the amount of fullerenes is varied, the absorbance increases more than linearly, which can be interpreted in terms of an increasing thickness per monolayer by increasing the amount of fullerenes in the solid film. This is confirmed by small angle x-ray measurements and ellipsometry. The thickness of the pure polymer used is 1.66 nm per monolayer whereas the thickness of a mixed layer with 50% fullerenes increases to 2.05nm per monolayer.

We also investigated the nonlinear optical properties of mixed films. The $\chi^{(3)}$ value for a film containing 100% fullerenes calculated from a linear extrapolation is $2 \cdot 10^{-11}$ esu.

*P. Häussler, H. Bestgen, H.-U. ter Meer,
Proceedings of the MRS-Spring Meeting, San Francisco 1992

Studies of the Flow of Condensed Langmuir Monolayers

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The technique of applying a grid of sulphur particles to a condensed monolayer to enable flow to be observed (Ref. 1) has been developed as a quantitative tool. This has been applied to measure the extent of nonuniformity of compression produced when polymer monolayers are compressed in a conventional Langmuir trough with sliding barriers.

Three polymers have been studied to give a range of monolayer rigidity: polybutylmethacrylate (PBMA), α -helical poly-L-alanine² (P-L-A1) and helical amylose-triacetate (ATA)³. A square 1 cm grid of sulphur particles was applied to the condensed monolayer at an area A_1 and the monolayer was then slowly compressed to A_2 , A_3 , etc. Large-size photographs at each stage were analysed by measuring the area of units, initially $3 \times 3 \text{ cm}^2$ on A_1 , over the whole surface. The values of A_2/A_1 etc. were then compared with corresponding values for the individual units and the results plotted to show their distribution over the surface.

Typical values obtained are as follows:

PBMA.	$A_2/A_1 = 0.71 \text{ :- } 0.67 \text{ to } 0.73$
P-L-A1.	$A_2/A_1 = 0.72 \text{ :- } 0.65 \text{ to } 0.77$
ATA.	$A_2/A_1 = 0.78 \text{ :- } 0.63 \text{ to } 0.88$

Further compression showed an increased range. Because it was necessary to compress the monolayer before sulphur particles were applied, these values underestimate the full range of the effects observed. Re-expansion of the monolayers has also been studied.

The results can be understood qualitatively in terms of the way the sides of the trough and the moving barrier affect the flow. In the case of PBMA the moving barrier causes stationary monolayer at the sides to flow inwards from the corners. This effect is less with more rigid monolayers giving rise to excess compression at the corners. These results show that the compression of a condensed monolayer on a standard Langmuir trough can be far from uniform. This is a fundamental limitation of the design, and the accuracy claimed for certain types of measurements with such instruments is questionable. To avoid the effects of sliding barriers, compressing monolayer within a folding rectangular frame is an alternative method that gives homogeneous compression⁴.

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4. B R Malcolm, Thin Solid Films **178**: 191-196. (1989)

SLOW STRUCTURAL REARRANGEMENT OF A SIDECCHAIN PHTHALOCYANINE POLYMER AT THE AIR-WATER INTERFACE

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A polymethacrylate with dodecoxy-substituted phthalocyanine sidechains (Fig. 1) forms a Langmuir-Blodgett monolayer at the air-water interface. This monolayer was not stable and expanded during a period of approximately 16 hours. During this time the occupied area per polymer repeating unit increased from 67 Å to 120 Å. Electron micrographs revealed that smooth domains of homogeneous thickness are present before expansion, and much smaller domains with a rough, grainy and more irregular surface appear after expansion. It was possible to record an electron diffractogram from the non-expanded monolayer but not from the expanded one, suggesting that the former layer has a high degree of crystallinity. From the diffraction pattern a rectangular unit cell of 16.6 Å x 3.9 Å was derived. Assuming one polymer repeating unit per unit cell the area occupied by a polymer side chain is 64.7 Å², which is in agreement with the value calculated from the pressure-area isotherms. From these results it is concluded that the polymer chain at the air-water interface initially has a conformation as schematically depicted in Fig. 2a.

Deposition of both the non-expanded and expanded monolayer onto various substrates was achieved with Y-type transfer by mixing the polymer with arachidic acid. FT-IR measurements on these multilayer samples show that the orientation of the phthalocyanine units had not changed during expansion. The visible absorption spectrum show a red-shift of the absorption maximum of the expanded film, indicating a decrease of interaction between the phthalocyanine units. From ellipsometry measurements on the expanded multilayer samples we could derive a single layer thickness of 28.8 Å. From these findings we propose that the polymer chain in the expanded monolayer at the air-water interface has a structure as shown in Fig. 2b. The observed expansion probably is the result of a change in the orientation of the periferic alkoxy chains, causing the more hydrophilic phthalocyanine core to become exposed to the water surface.

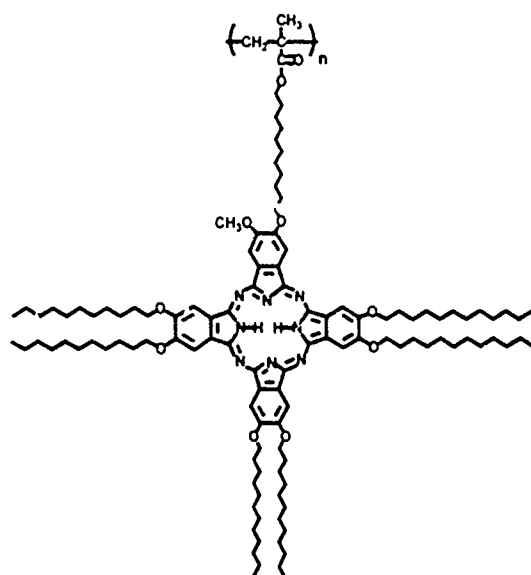


Figure 1

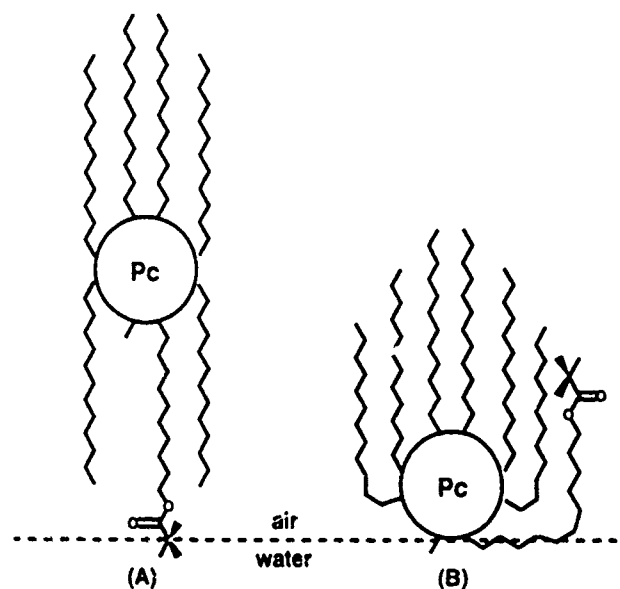


Figure 2

PREPARATION OF LANGMUIR-BLODGETT FILMS FROM AN AZO-BENZENE DERIVATIVE

B. B. Stefanov, G. R. Ivanov, J. Petkova, A. G. Petrov, and D. Tsankov*

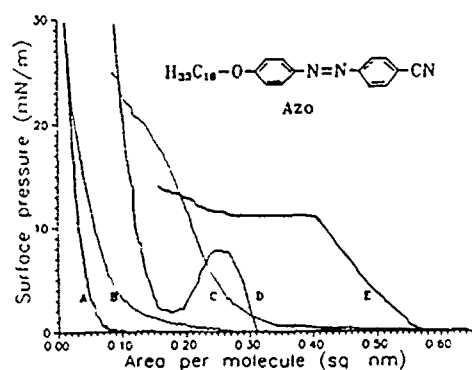
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Azo-benzene derivatives are promising candidates for non-linear optics, optical data storage, sensors applications and several new effects have been found in them. The investigated compounds exhibit different behaviour at the air-water interface depending on the preliminary irradiation with UV or VIS light and the compression velocity (Fig. 1). The irradiation of the solution with UV (365 nm) light transfers the Azo almost completely in cis-conformation (Fig. 2) but during the subsequent transfer part of the molecules go back in trans-conformation. The non-irradiated structures are amorphous on transfer while the irradiated structures exhibit the morphology shown in Fig. 3 and slight H-aggregation (Fig. 2). The UV irradiated Azo can be transferred as Z type LB film while the VIS irradiated Azo forms 3 layers on top of one another at the air-water interface at pressures above 10 mN/m. This configuration can also be successfully transferred. The LB films were characterized by polarized UV-VIS and FTIR spectroscopy exhibiting relatively low ordering of the chromophores. Mixtures with arachidic acid and dipalmitoyl phosphatidic acid were investigated and transferred. This work was supported under contracts MU-NM-12 and F-19 with the National Science Foundation.

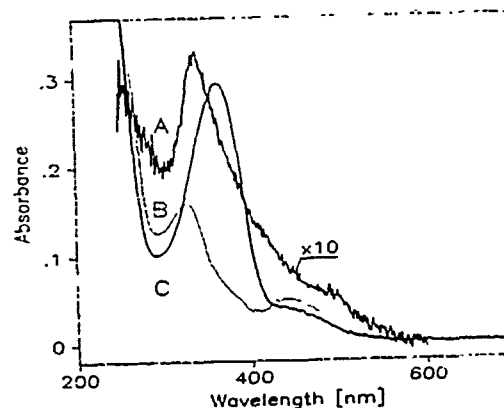
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Curves A, B and C: nonirradiated solution, curve D: VIS irr. solution; curve E: UV irr. solution, Compression rate: A - 5×10^{-2} nm²/s; B, D, E - 10^{-3} nm²/s; C - 5×10^{-4} nm²/s

Fig. 1



A - 17 monolayers cis Azo (Z type) at P = 10 mN/m; B - UV irr. solution; C - nonirr. solution

Fig. 2

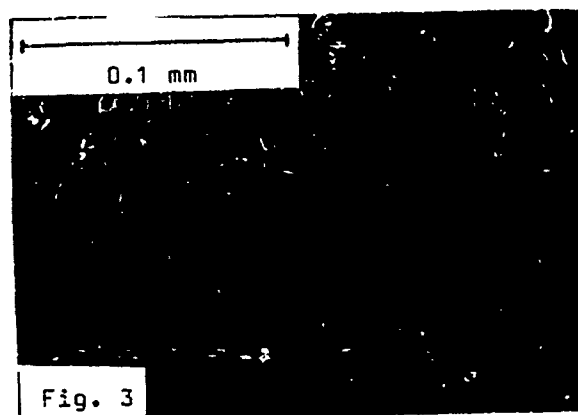


Fig. 3

DEPENDENCE OF THE MULTILAYER - WATER pK_i ON THE NUMBER OF DEPOSITED MONOLAYERS

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Abstract

Fluorometric titration of the interfacial pH-indicator 4-heptadecyl-7-hydroxy coumarin, incorporated in a neutral methyl arachidate monolayer, has been performed at the solid/liquid interface. The matrix monolayer with the fluorescent probe has been deposited onto siliconized glass substrate covered with cadmium arachidate multilayers of different thickness. Large and long-range effect of the spacer multilayer thickness has been observed - after an increase of 2.5 units the multilayer/water pK_i reached a saturation at a thickness of about 250 Å. This dependence seems to be due to the existence of a double layer of free charge carriers in the spacer multilayer. Such an influence of the inner phase on the interfacial pK_i should be taken into account in the applications of the fluorescent probe method for determination of the ϕ^0 -potentials of micelles, vesicles and Langmuir-Blodgett assemblies.

INTERACTION FREE ENERGIES OF LANGMUIR - BLODGETT MULTILAYERS OF DOCOSYLAMMONIUM PHOSPHATE

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Abstract

The influence of pH and ionic composition of the phosphate subsolution on the static contact angles during Langmuir-Blodgett deposition of docosylammonium phosphate is studied. The free energy of interaction of the hydrophylic head groups, ΔG , is evaluated and compared with theoretical estimates of the van der Waals, ΔG_{vw} , electrostatic, ΔG_e , and structural, ΔG_s , components. The analysis shows that the sum of ΔG_{vw} , ΔG_e and ΔG_s is positive, while the experimental interaction free energy is negative. This discrepancy leads to the conclusion that some strong, short range attraction was neglected in the above energetic balance. Our previous IR-spectroscopic data show that this attraction might be attributed to hydrogen bonds between the opposite ammonium groups and the phosphate counter-ions included between them. These bonds cause dehydration of the groups involved and probably ensure the head-to-head adhesion in the LB-multilayer.

An alternative interpretation of the above discrepancy takes into account the attractive ion-correlation free energy, which might be prevailing compared to all other components in the case of divalent counter-ions. Discrimination of the two attractive contributions is impossible so far because of their incomplete theoretical description.

INTERACTION OF LONG - CHAIN AMINE MONOLAYERS WITH POLIVALENT COUNTER - IONS FROM THE AQUEOUS SUBSOLUTION

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Abstract

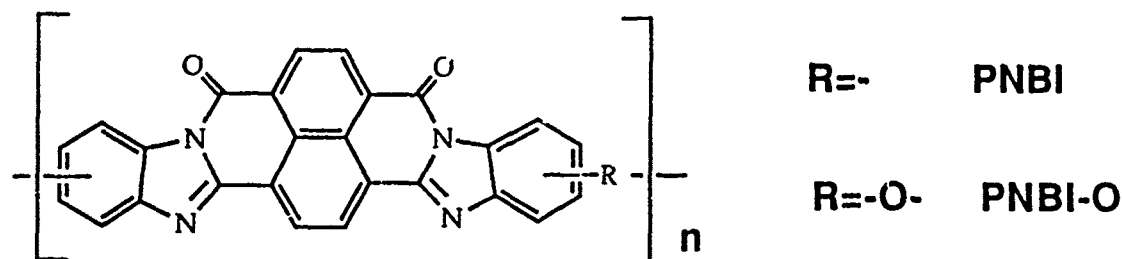
The amount of phosphate and chromate anions in Langmuir - Blodgett multilayers of docosylamine was studied by means of neutron-activation and atomic absorption analysis. The pH - dependences of the number of counter-ions per amine molecule, ϕ , were obtained and compared with our previous results for LB-films of docosylammonium arsenate (Angelova and Petrov, Langmuir, 1992) and for porphyrine adsorption on eicosyl amine monolayers at the liquid/gas interface (Möbius and Grüniger, Bioelectrochem. Bioenergetics, 1984). The monolayer/counter ion interaction was found to be non-specific in the alkaline pH-range and specific in the acidic pH-range - all four ϕ /pH dependences coincide within the limits of the data scattering above pH 6.0 and below this value they have different trends. These results are interpreted on the basis of the electrostatic character of the interaction, the similar tetrahedral structure of HPO_4^{2-} , HAsO_4^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and of the charged SO_3^- - groups of the porphyrine, and the steric hindrance in the cases of dichromate and porphyrine anions.

The Structure of Poly(naphthoylene benzimidazole) -Stearic Acid Mono- and Multilayers

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Poly(naphthoylene benzimidazole)s are a ladder type polymers:



They possess an outstanding thermal stability (up to 600°C), high mechanical (strength and modulus) and third order nonlinear optical properties in the bulk /1/. The latter is conditioned by their long range system of π -electron delocalization. Such polymers can be prepared from the soluble prepolymer via polymer-analogous reaction - thermocyclization /2/.

We have investigated the behaviour of PNBI and PNBI-O prepolymers at the water surface - π -A isotherms. It was shown that attaching of 0.5 to 2 stearic acid (St) molecules per monomer of pre- π -A (formation of stearic acid salt) improves the stability of monolayers at the water surface and thus allows the LB films deposition. The multilayer systems obtained were investigated by means of X-ray diffraction direct after deposition on the glass or silicon substrates as well as after the thermal treatment of the samples. During the annealing at 100- 350°C the desorption of St molecules and cyclization of polymer backbone occur leading to superthin (in fact, with the atomic thickness per monolayer due to the flat form of polymer molecules and strong intermolecular interactions) insoluble thermostable film formation. The peculiarities of cyclization reaction leading also to long conjugated chain creation in the system can be controlled by optical absorption.

/1/ D.R.Ulrich, Polymer, 1987, **28**, N 4, p.533

/2/ N.V.Pogodina et al, Polymer Sci.USSR, 1989, **31** A, N1, p.73

On the Nature of Specific Interactions and Adhesional Forces Between Langmuir
Monolayers and Various Substrate Interfaces

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The interactions between Langmuir monolayers of fatty acids or lipids and various hydrophilic substrates are investigated as function of different monolayer parameters (surface pressure, temperature, etc.). The adhesion is quantified by contact angle measurements which are performed at the three-phase line with the transfer fluorescence microscope. The correlation between structure and adhesion of transferred monolayers is also studied by electron diffraction.

Morphological Instabilities and Condensation Microstructures in Langmuir Monolayers at the Air/Water/Substrate Three-Phase Line

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Morphological instabilities and solidification microstructures in Langmuir monolayers at the air/water/substrate three-phase line of a typical LB-transfer configuration are investigated by transfer fluorescence microscopy. The breakdown of the linearity of the condensed/expanded phase line, directional fingerlike cell growth, and dendritic growth are studied as function of various parameters (compression speed, temperature, dye concentration, substrate preparation, etc.). By compression of the monolayers above 30 mN/m and following pressure reduction it is possible to interconnect the liquid-condensed phase and generate a phase-contrasted monolayer with liquid-expanded domains embedded in the liquid-condensed phase. Thus a direct comparison between morphological growth phenomena at a straight line without the influence of heterogeneous nucleation (at the three-phase line) and with heterogeneous nucleation and substrate influences (at the three-phase line) is made possible.



Nucleation and fingering condensation at the three-phase line (DMPE, 20°C, SiO₂)

- [1] Hans Riegler and Karl Spratte (1992), *Thin Solid Films* 210/211:9-12
- [2] Karl Spratte and Hans Riegler (1991), *Makromol. Chem.; Macromol. Symp.* 46:113-123
- [3] Hans Riegler and Karl Spratte (1990), in A. Blumen, J. Klafter and D. Haarer (eds.) *Dynamical Processes in Condensed Molecular Systems*, World Scientific, London, 105-115

CONTROLLING THE STRUCTURE AND MORPHOLOGY OF 2-DOCOSYLAMINO-5-NITROPYRIDINE (DCANP) FROM THE MICROSCOPICAL TO THE AFM SCALE

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Multilayers of DCANP display the interesting feature of showing second harmonic generation (SHG) in a non-alternating, Y-type arrangement. In fact DCANP was used to fabricate the first polar waveguide by the LB-technique. The polarity in the LB-film arises from a "herringbone"-structure in the multilayer /1/, which was also observed in LB-films of similar amphiphiles /e.g. 2/. For future applications the ability to control and manipulate the structure and morphology of LB-films is of critical importance.

Here, LB-films of DCANP have been investigated using optical microscopy, atomic force microscopy (AFM), UV/Vis-spectroscopy and small angle X-ray scattering (SAXS).

RESULTS

The influence of the spreading solvent on the morphology of the deposited multilayer is demonstrated in Fig. 1, where the AFM-images of 30 layers DCANP on silicon are shown.

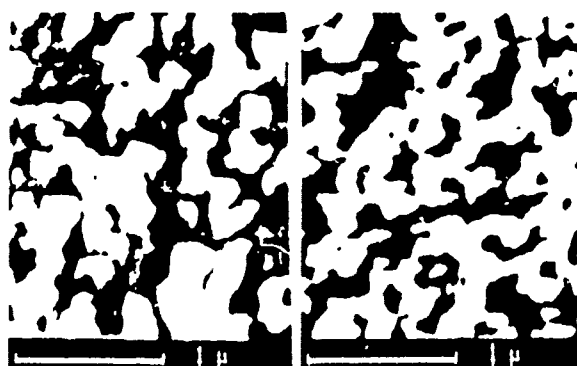


Figure 1: AFM-images of 30 layers DCANP deposited onto hydrophobized silicon (18 mN/m, $T=15^{\circ}\text{C}$). Spreading solvent: chloroform (left), hexane/ethanol (9:1) (right)

Upon heating (to 60°C or above) LB films of DCANP undergo a phase transition, which might be interpreted as the transition from a Y-type to a X-, or Z-type structure. This can be monitored easily using SAXS, as shown in Fig. 2, where a LB-film is held at 65°C for 50 minutes and then cooled to room temperature again. The initial d-spacing of 4.48 nm, corresponding to a "herringbone", Y-type structure, vanishes with time at $T=65^{\circ}\text{C}$, finally resulting in a d-spacing of 3.14 nm (slightly shorter

than the length of one molecule) which stays stable after cooling to room temperature.

Evidence for this structural rearrangement is also gained from UV/Vis-spectroscopy, where the spectroscopic properties of DCANP allow to detect the usual Y-type head-to-head contact between adjacent layers /3/. This loss of specific head-to-head interaction at $T = 65^{\circ}\text{C}$ is also clearly observed in the UV/Vis spectrum.

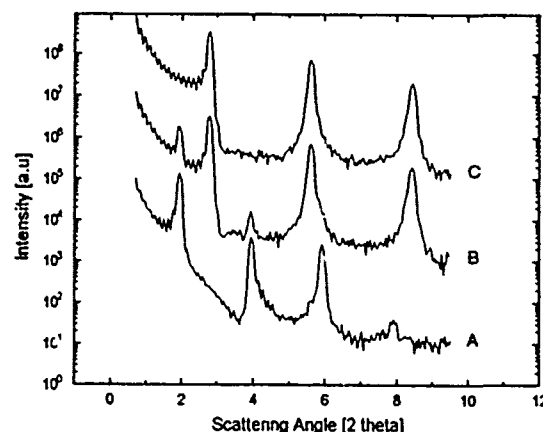


Figure 2: X-ray diffractogram of 30 layers of DCANP deposited onto hydrophobized silicon (18 mN/m, $T=15^{\circ}\text{C}$). Room temperature (A); $T=65^{\circ}\text{C}$, after 20 min (B); room temperature, after cooling (C)

AFM at molecular resolution yields a two-dimensional unit cell close to the one found in electron diffraction /4/.

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LANGMUIR-BLODGETT MULTILAYER FILMS OF WATER-SOLUBLE AMPHIPHILES DEPOSITED FROM POLYELECTROLYTE CONTAINING SUBPHASES

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INTRODUCTION

It is well established that amphiphiles of long-chain alkyl ammonium salts form a liquid expanded monolayer at the air/water interface. Because of the strong repulsive interaction of the ammonium-groups, which is not fully compensated by the counterions such as Cl^- or Br^- , these monolayers are rather difficult to transfer onto solid substrates/1/. Transfer could be facilitated by exchanging those small anions by polyanions contained in the subphase/2/. The multilayer structure of such polyion complex films has been studied in detail/e.g. 3/, they show enhanced mechanical and thermal stability and allow transfer of amphiphiles, which cannot be deposited alone/4/.

RESULTS AND DISCUSSION

We have extended this concept by stabilizing monolayers of water-soluble amphiphiles using the polyion-complex technique/5/. If classic water-soluble detergents, such as cetylpyridinium chloride (CPCl) or cetyltrimethylammonium bromide (CTAB) are spread on the surface of pure water, an expanded monolayer is formed. Upon compression of the film a rapid loss of area with time is observed, caused by material dissolving into the subphase. If the same materials were spread onto an aqueous subphase containing polyelectrolyte such as polyvinylsulfate (PVS), a water insoluble complex is formed at the air/water interface/5/ (Fig. 1).

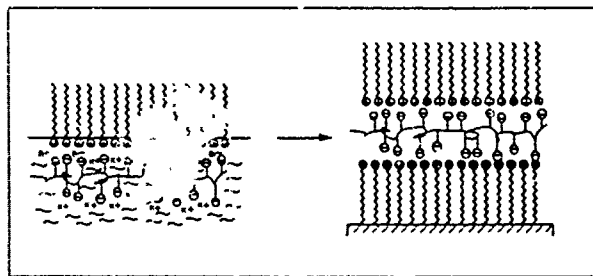


Figure 1: Schematic representation of a CTAB/PVS monolayer at the air/water interface and after transfer onto a solid substrate/5/.

The monolayers of the amphiphile/polyion complex can be transferred onto solid substrates such as hydrophobized silicon single crystals or fused quartz. The multilayer buildup was studied by UV spectroscopy (Fig. 2).

Small angle X-ray scattering (SAXS) of transferred multilayer films (Fig. 3) shows two reflections for the bilayer spacing of 37 Å, which indicates a good stacking of the layers. In the maximum extended conformation a

CTAB molecule has a length of 16 Å. This means that the polyelectrolyte layer, sandwiched between two CTAB molecules, has a thickness of at least 5 Å for the case of untilted CTAB-chains.

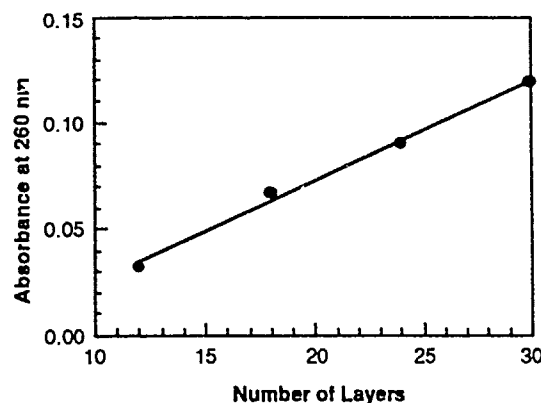


Figure 2: Linear deposition behavior of CPCl/PVS LB-film as monitored by UV-spectroscopy at 260 nm.

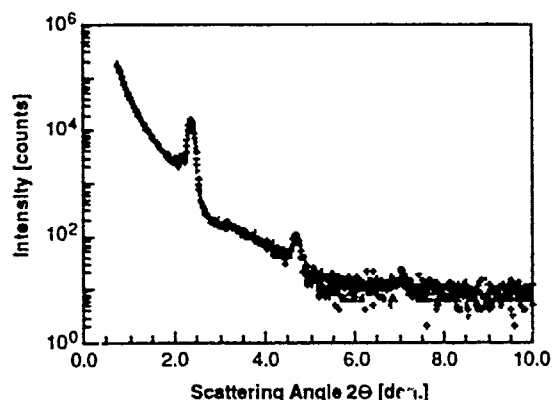


Figure 3: SAXS diffractogram of a 20 bilayer LB-film of CTAB/PVS

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LB-Deposition and Structure Investigation of Discotic Multiyne
Mesogens

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Langmuir-Blodgett-multilayers were prepared from disc-shaped multiyne mesogens based on amphiphilic alkyl pentakis(aryl-ethynyl)benzene ethers. The two compounds used are characterized by five hydrophobic flexible chains and one hydrophilic substituent at the terminal position of the alkoxy chain. The LB-films were analyzed by X-ray scattering and spectroscopical measurements. An edge-on arrangement of the two discotic pentaalkynes within Y-type bilayers with a different density of packing proved to be possible for the LB-films of both compounds.

Structural models of LB-films calculated from the experimental data based on BIOSYM® modelling software will be discussed. From these calculations one can draw the conclusion, that, for energetic reasons, the columnar molecular in-plane order should be favourable.

Corrections of the Intensity of X-ray Diffraction for Langmuir-Blogett Films

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X-ray diffraction experiments on Langmuir-Blogett (LB) films are commonly used to obtain bilayer spacings. However, the intensity data can also be used to calculate electron density profiles perpendicular to the membrane normal.

Such kind of analysis requires 'ideal' intensities, whereas, generally the measured intensities are not 'ideal' so that corrections are necessary.

Usually applied corrections to measured X-ray intensities are the Lorenz/polarisation and a factor proportional to the order of reflection. However, we obtained evidence that this might not suffice for thin LB-films for which a considerable number of reflections can be observed at large scattering angles. In such cases a better agreement between theoretical and measured intensities was obtained by correcting the measured intensities by an additional geometry factor. This factor accounts for the width of the LB slide and the slit-width of the X-ray beam.

We will present a series of X-Ray diffraction experiments on stearic acid, measured as Langmuir-Blogett films and also as crystalline powder. In the crystals the stearic acid is in the B-form.

Since the structure of stearic acid in the B-form crystals is known in atomic detail, the theoretical scattering intensities could be evaluated with the program MEMBRANE. The simulated intensities corresponded well to the experimental intensities corrected with the additional geometry factor. Without use of this correction, the evaluated electron density profiles seemed to be less resolved. This indicates that the use of the correction factor is important for a correct interpretation of the fine structure of electron densities.

In another series of measurements, LB-films of Ba-stearate of different geometry, i.e. with varying width and length of the covered slides, were investigated. From these experiments, further evidence for the intrinsic correctness of the new geometric factor was obtained.

The important conclusion was drawn for the scaling of sets of different measurements of the same sample with varying slide-width that it does not suffice to normalize two different sets to the height of a common reflection. Instead of this, the additional geometry factor has to be applied before.

Mixed Alkanethiol Monolayers on Gold Surfaces: Substrates for Langmuir-Blodgett Films Deposition

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Self-assembled monolayers (SAMs) of mixed alkanethiols have been used as substrates to study the deposition process during Langmuir-Blodgett film formation. Not only do they provide a unique way of controlling the substrate (surface) properties, and hence their effects on film deposition, but they also facilitate the formation of high quality LB films on gold (a substrate proven to yield un-reproducible results for LB film formation).

Measurements of the deposition ratio and dynamic contact angles were taken during the transfer of an Arachidic acid monolayer from the air-water interface to the SAM-coated substrates. The contact angles were obtained by imaging the three-phase line. By varying the ratio of polar (OH) and non-polar (CH₃) groups in the substrate surface one can effectively vary the work of adhesion between the subphase and the substrate. The work of adhesion is proportional to the cosine of the contact angle and is dependent on the surface concentration of -OH.

An abrupt transition was found in the value of the deposition (transfer) ratio as a function of the surface OH concentration. The transition which occurs in the region between 30 and 40% surface-OH concentration, is similar to the wetting transition found for hexadecane on the same surfaces.¹ The occurrence of the transition at the same OH concentration as found previously suggests that the prewetting adsorbed water film, present on these surfaces, may be necessary for high deposition ratios, on the outward stroke. Correlation between the deposition ratio and the contact angle shows that contact angles smaller than 30° give rise to deposition ratios close to unity. (in agreement with recent results reported by Aveyard *et al.* ²)

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STRUCTURAL STUDY OF L.B. FILMS OF A RIGID-ROD POLYMER BY X-RAY
DIFFRACTION

AP17

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The structural study of L.B. films by X-ray diffraction is generally hampered by the thickness of the deposition substrate which restricts the possible scattering geometry to the reflection configuration. In order to work also in the transmission configuration, ultrathin silicon wafers have been used as substrate (thickness: 10 μ m). The kind of results that can be obtained in such a way is exemplified in the present poster with L.B. films of a rigid-rod polymer (phthalocyaninato polysiloxane with alkyl side chains). This polymer has been previously shown to yield films of high optical quality and perfectly well-defined thickness.

As drawn films: A surprising result is the absence of well-defined layers within the film: indeed the structure can be compared to the one of a nematic liquid-crystal. The polymer rods lie flat on the substrate and are locally parallel to each other. An average distance between the rods and the corresponding correlation length can be determined for every direction between the parallel and perpendicular to the substrate. Furthermore the orientation of the nematic domains with respect to the dipping direction has been also precisely determined.

Annealed films: Upon annealing (180°C) the packing of the polymer chains becomes hexagonal, without degradation of the film quality. The relevant parameters have been accurately determined. Evidences of a helicoidal conformation of the polymer backbones are also given.

The Influence of Counterions and Hydrophobic Moieties on the Thermostability of LB Multilayers

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Langmuir-Blodgett multilayers with various counterions (divalent and trivalent) and different organic moieties (one- and two-chain fatty acids) were prepared to investigate structural changes and thermodesorption by temperature dependent Small Angle X-Ray Scattering (SAXS), Interference-enhanced Reflection (IeR) and Normasky microscopy.

On temperature increase a sequence of phase transitions can be observed: A crystalline LB-film melted to a fluid phase and eventually desorbed either from droplets or from a homogeneous film.

The phase sequence depends on the counterion:

Ferric Stearate and Nickel Stearate melt while the layered structure is conserved; SAXS - measurements show a continuous decrease of the layer-spacing as well as the total film thickness:

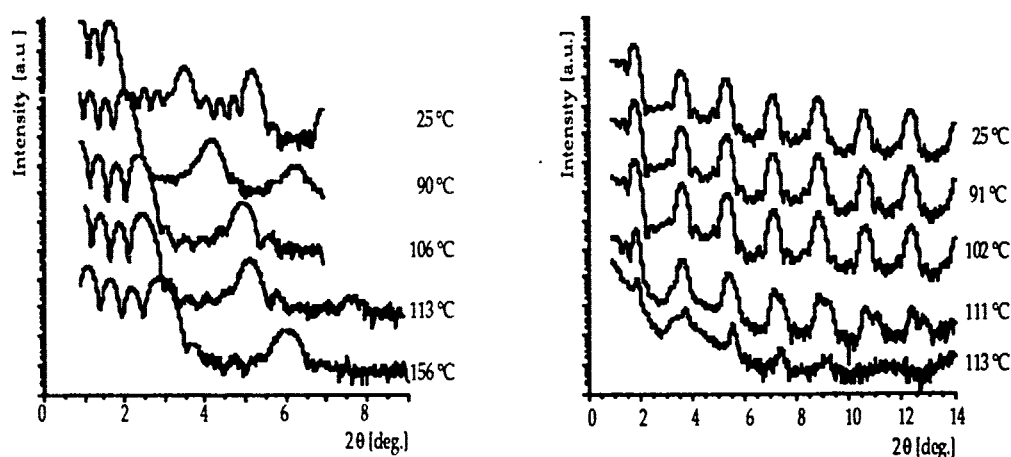


Figure 1: X-ray diffractograms of 11 layers of Nickel Stearate (left) and 12 layers of Lead Stearate (right) at different temperatures.

Lead Stearate exhibits the opposite behaviour: before rupturing, a coexistence of two phases is observed.

These general features do not depend on the substrate (pure Silicon or silanized silicon), the coating only influences size and lateral distribution of the droplets.

Salts of a double chained fatty acid show a decreased thermal stability. This may be due to a heteroatom (nitrogen) within the chain or the decreased density of the stabilizing metal ions.

Mixed layers of stearic acid and the double chained compound prepared on a lead subphase differ in the temperature of rupturing as well as the distribution of the formed droplets.

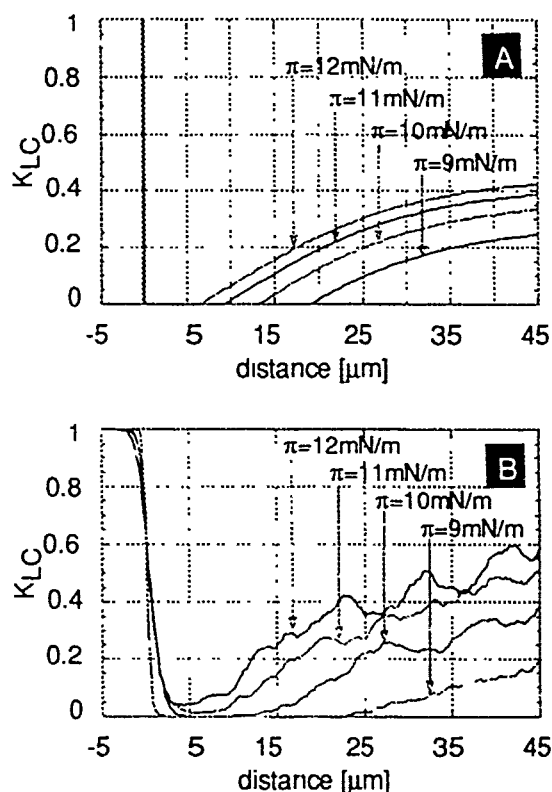
Structural and Compositional Variations in Monolayers Before, During, and After the LB Transfer as Result of Substrate-Layer Interactions

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The local variation of the morphology and composition of a monomolecular film (Langmuir monolayer) is investigated adjacent to the three-phase line where the monolayer touches the substrate. The monolayer is studied via transfer fluorescence microscopy in a typical Langmuir-Blodgett transfer configuration, where the film extends from the plane water surface over the meniscus region onto the solid substrate while it is continuously transferred onto the solid carrier. The monolayers consist of a mixture of amphiphilic lipid molecules (solvent) with minor amounts of a fluorescing dye (solute). These monolayers undergo substrate-mediated condensation during the transition from the floating subphase to the solid subphase. Well known three-dimensional models are modified for the situation of the monolayer transfer and thus details of the local dye distribution and monolayer morphology are derived theoretically. This approach analyses the mixed monolayer in a general way as a two-dimensional alloy undergoing a phase transition between two states of different solute solubility (monolayer on the water vs. monolayer on the substrate). Thus a local dye concentration variations and various morphological alterations are predicted. Comprehensive experimental results qualitatively and quantitatively corroborate the proposed model. Thus it is demonstrated that Langmuir monolayers are excellently suited to study general proper-

ties of local compositional and morphological variations in two-dimensional systems undergoing phase transitions.



Liquid-condensed area fraction K_{LC} as function of the distance from the three-phase line for four different surface pressures. Figure A shows K_{LC} calculated according to the proposed solidification model. Figure B shows the experimentally measured K_{LC} as function of the distance from the three-phase line for four different pressures. The fit-parameters used in Figure A correspond to the conditions of the experiments shown in Figure B.

[1] Hans Riegler and Karl Spratte (1992), Thin Solid Films 210/211:9-12

[2] Karl Spratte and Hans Riegler (1991), Makromol. Chem.; Macromol. Symp. 46:113-123

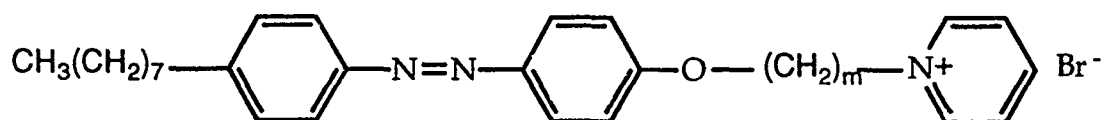
[3] Hans Riegler and Karl Spratte (1990), in A. Blumen, J. Klafter and D. Haarer (eds.) Dynamical Processes in Condensed Molecular Systems, World Scientific, London, 105-115

Cis-Trans Isomerization Of Azobenzene Amphiphiles At The Air/Water Interface

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We have investigated the degree and kinetics of photoinduced cis-trans isomerization of azobenzene amphiphiles of the general structure $C_8AzoC_m py^+$ (shown below ; $m = 12, 14, 16, 18, 20$) in monolayers at the air/water interface using surface pressure-, and surface reflection-area isotherms along with the UV-VIS spectroscopy and Brewster angle microscopic and reflectometry techniques. The cis-trans isomerization process leads to reversible changes in surface pressure, reflection spectrum and Brewster reflectivity. It was found that the degree and kinetics of cis-trans isomerization depends sensitively on the length of spacer (value of m) and the surface density or pressure.



The reflection spectra of the pure azo amphiphile monolayers show blue shifts upon compression, indicating formation of dimers and H aggregates which adversely affect the reversibility and the degree of cis-trans isomerization. However, if the monolayer is prepared on subphase containing polyelectrolytes such as polystyrene sulfonate, the tendency to form aggregates is decreased. These and other results are discussed in terms of molecular orientation, packing, aggregation and complexation of head group pyridinium with polyelectrolytes in the subphase.

Characterisation of Langmuir-Blodgett Films with the Atomic Force Microscope

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ABSTRACT

The atomic force microscope (AFM) has been used to image multilayer Langmuir-Blodgett (LB) films of trans-6-octadecenoic acid deposited on an amorphous glass plate. The two dimensional fast fourier transform analysis of the AFM image together with the consecutive inverse transform is suggested for obtaining the salient structural packing features of the LB films. Comparison of four different types of cantilevers is given. Well ordered periodic structures with molecular resolution could be obtained by using a cantilever with a spring constant of 0.38 N/m. Some of the cantilevers proved to be clearly incompatible for LB film imaging.

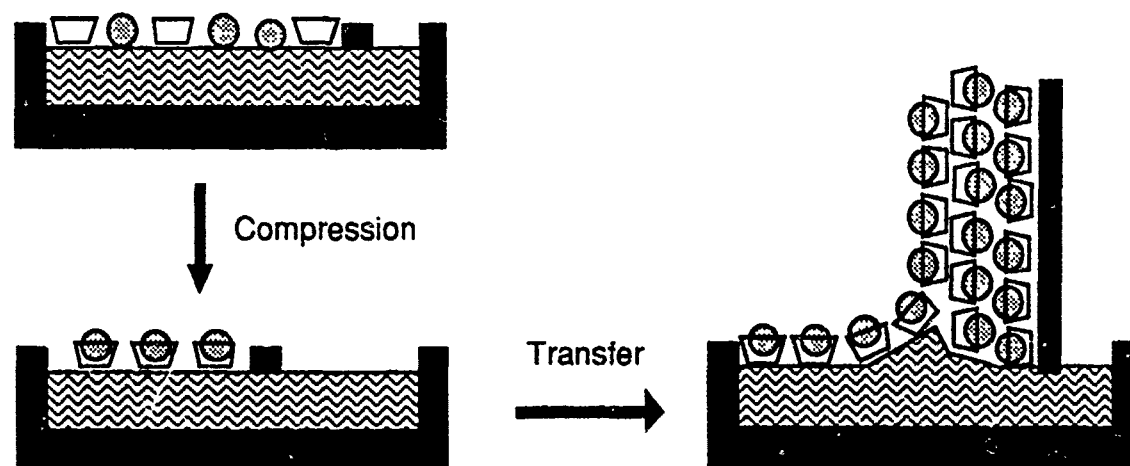
The molecularly resolved images of the LB films studied showed the characteristics of liquid crystalline phases with density fluctuations and several dislocations found on areas typically of the size $100 \times 100 \text{ nm}^2$. The packing symmetry varied with the counterion used. The use of Tb^{+} counterions seemed to lead in a two-plane packing within a monolayer whereas the use of Cd^{2+} counterions resulted in a packing system where all the monolayer molecules lie in a single plane. Finally, the effect of UV-irradiation on the film structure was studied. The irradiation was found to generate irregularities and even cracks in the surface but still some order remained in the film.

Supramolecular Structures with C₆₀/C₇₀ in Mono- and Multilayers

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The Fullerenes C₆₀ and C₇₀ are interesting partners for building supramolecular structures at the air-water interface with cavity-containing molecules. Functionalized azacrowns, calixarenes and cyclodextrins are such basket-shaped molecules which should be capable to accommodate the fullerenes and form monolayers at the water surface. The spreading behaviour of the pure compounds and the mixtures was investigated and the monolayers could be transferred to solid substrates. The resulting LB-multilayers were characterized by SAXS, UV spectroscopy, AFM measurements and other methods. In all cases the fullerenes stabilize the monolayers and enhance the quality of the multilayers. Whether the "bucky balls sit in the bowls" or not, as suggested by the following scheme, will be discussed at the poster.



Monolayer behaviour and LB-transfer of poly(4-vinylpyridinium) type polyelectrolytes

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Quaternization of poly(4-vinylpyridine) with long-chain n-alkyl bromides [1] yields water-insoluble amphiphilic polyelectrolytes. Degrees of alkylation were 39 (O39), 59 (O59) and 93 % (O93) with octyl bromide, 34 (D34), 70 (D70) and 97 % (D97) with dodecyl bromide and 23 (C23), 53 (C53) and 96 % (C96) with cetyl bromide. The monolayers show increasing stability in concern of desorption with degrees of alkylation and side-chain lengths.

Isotherms of all dodecyl-derivatives, high-alkylated octyl- and low alkylated cetyl-derivatives show a first order transition from a fluid to a rigid phase (fig. 1), indicated by a more or less flat plateau region of film pressure. With good approximation the area at the end of the plateau region corresponds to half of the area at the beginning of the plateau region. Maintaining film pressure constant over time just below the plateau leads to spontaneous relaxation of the area per monomeric unit to one half of the initial area (fig. 2). Furthermore, quartz microbalance weighing of layers transferred just after plateaus show double mass deposition compared to deposition just before plateaus, revealing that desorption of monolayers can be excluded. These results are good evidence for double layer formation on phase transition.

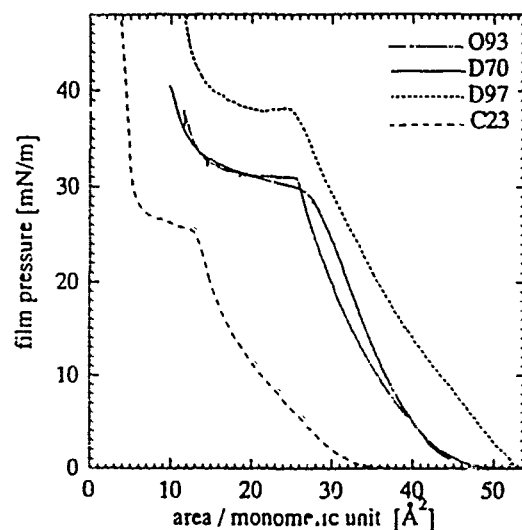


Fig. 1: Typical π/A -isotherms showing first order phase transitions. Note reduction of areas to a half on running through film pressure plateaus.

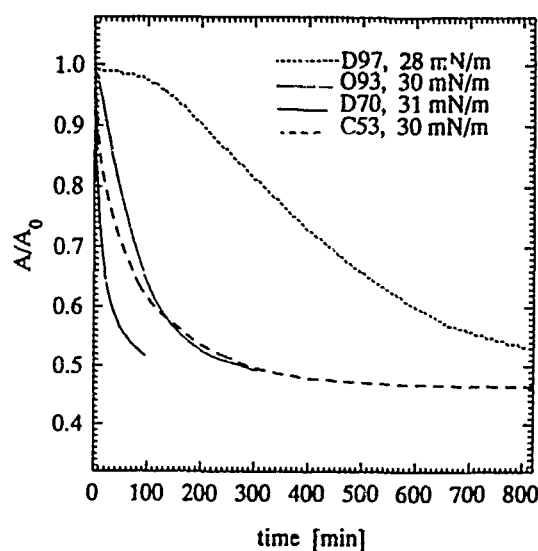


Fig. 2: Reduction of area / monomeric unit on maintaining constant film pressure somewhat under plateau film pressures.

but low alkylated octyl-derivative can be transferred to LB-multilayers. While deposition on the upward passage is quantitative for all substances, it is highly dependent on the degree of alkylation and side-chain length on downward passage of the substrate. Exceptionally good deposition characteristics are obtained with high-alkylated dodecyl-derivative, which can be transferred at relatively high deposition speed (50 mm per minute and more), the plot of ellipsometrically determined film thickness versus number of layers is of perfect linearity.

Ellipsometric study of LB-film thickness of highly quaternized substances reveal an orientation perpendicular to the substrate surface.

P O S T E R S

SESSION B: BIOLOGICAL

Tethered and Mobile Supported Bilayers as Model Membranes

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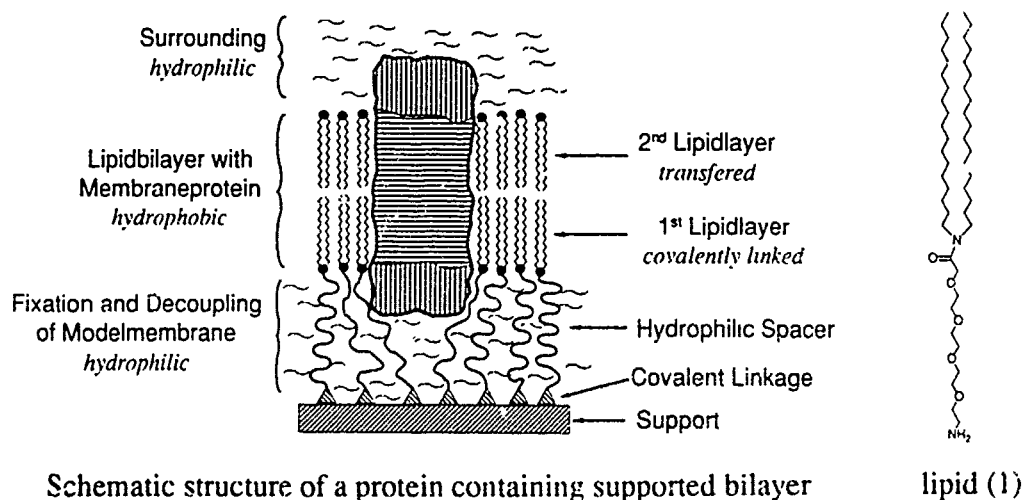
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Biological membranes are characterized by a bilayer arrangement of the lipids combined with a certain mobility of the lipids within the membrane. To model biomembranes liposomes (high mobility, low stability) or planar systems, e.g., LB-layers (high stability, low mobility) are widely used.

This poster presents an approach to combine the inherent advantages of liposomes with planar model membranes, i.e., to build up a stabile supported bilayer retaining the mobility.

In the present case stability is achieved by fixation of the first monolayer to the substrate and mobility by introducing a water layer, bridged with hydrophilic spacers, between bilayer and substrate. The water layer in addition should prevent denaturation of incorporated membrane proteins at the support.



To build up this structure lipids with different ethylenoxide spacers and terminal amino groups were synthesized, e.g., lipid (1) and characterized at the gas/water interface. These monolayers can be transferred and linked onto different substrates. Ionic fixation is achieved by the mica/amine pair, for covalent fixation on glass/ silicone/ quartz the substrates were first covalently covered with a monolayer of isothiocyanate bearing silane that forms thiourea with amines. Afterwards the second lipid layer is transferred via LB-technique. This technique allows to build up bilayers of arbitrary composition using the surface reactive lipids as anchor groups to the support. Especially the use of functional lipids, e.g., Biotin lipid followed by Streptavidin docking may lead to protein monolayers on a solid support.

The stability and the influence of the spacer and different substrates on the first layer were studied by water contact angle measurements. Bilayers were investigated using fluorescence microscopy and FRAP measurements. These techniques allow to detect the mobility within the layer.

The Incorporation of Channel Forming Proteins into Langmuir Blodgett Films of Phosphatidic Acid.

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The incorporation of the channel forming protein mixture gramicidin D into multilayer dipalmitoyl phosphatidic acid films has been achieved by the co-deposition of a 16:1 lipid: protein mixture over a subphase of ultra pure water using the Langmuir Blodgett technique. Over 100 layers of the mixture have been produced with a deposition ratio of 1 ± 0.1 maintained throughout the experiment. The Films have been examined by ellipsometry and FTIR spectroscopy, and are shown to be highly ordered with the alkyl chains of the lipids at an angle of $75 \pm 3^\circ$ to the substrate.

The isotherm of the 16:1 mixture shows only one inflection point (at 20 mNm^{-1}) and we believe this to correspond to the rearrangement of the gramicidin on the water surface. The average area per molecule at the dipping pressure can be seen from the isotherm to be 50 \AA^2 . If the area per molecule of DPPA is assumed to be 42 \AA^2 then the calculated area of gramicidin would be 180 \AA^2 . Within experimental error this is in agreement with the values recorded for the active form of the channel. In the FTIR experiments an intensity enhancement for the stretching vibrations (amide A, and amide I) is seen in RAIRS: this is consistent with a helical structure oriented perpendicular to the membrane (parallel to the membrane normal). Potential applications of this novel structure in the field of sensors and molecular electronics are discussed, and a detailed analysis of the IR spectra will be given.

Monofilm and X-ray Diffraction Investigations of the Amphiphilic Constituents of the Cytoplasmic Membrane of *Staphylococcus aureus*

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Biological membranes present a variable mixture of certain amphiphilic compounds. These amphiphiles create a powerful protection against harmful substrates, against lysis and serve as effective matrix for membrane located proteins. In gram-positive bacteria one finds simple anionic phospholipids, cardiolipin and glycosyldiglycerides and the complex amphiphiles of lipoteichoic acids (1,2). The structural properties of those bacterial amphiphiles are not well investigated. Possible changes in the biophysical properties of the obtained membranes, induced by certain amphiphiles, are less examined up to know.

To gain more insight into the structural and biophysical properties of the cytoplasmic amphiphiles of gram-positive bacteria, we have investigated by X-ray diffraction and monofilm measurements the amphiphiles phosphatidyl glycerol, cardiolipin, diglycosyldiacylglycerol and lipoteichoic acid isolated of *Staphylococcus aureus*. The hydrophobic portion of the examined lipids here is a mixture of different iso and anti-iso fatty acids with a chain length between 14 and 20 methyl groups. A similar composition of the fatty acid chains is also found in isolations of lipoteichoic acid, by varying length and substitution of the polyglycerophosphate chain (3).

In the X-ray diffraction experiments self assembled multilayers of the single compounds all showed a bilayered arrangement, except lipoteichoic acid. Reflections up to fifth order could be found. Monofilms of the amphiphiles showed a uniform π/A -isotherm without distinct phases. Change of subphases had only minor effects on the obtained isotherms.

By the addition of lipoteichoic acid to the different amphiphiles several effects could be observed. In all X-ray measurements a drastic decrease in the ability to form bilayered arrangements was observed, except in the case of diglycosyldiacylglycerol. In the obtained monofilms of the bacterial amphiphiles mixed with lipoteichoic acid, the stability of the monofilms is weakened on increasing amounts of the acid. Furthermore immiscibility of both amphiphiles is detected at higher concentrations of lipoteichoic acid and at increasing lateral pressure.

The obtained data of the described measurements will be presented and the structural properties and biophysical effects on bacterial cytoplasmic membranes will be discussed.

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MONOLAYERS OF LPS EXTRACTED FROM ROUGH MUTANT BACTERIA

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Abstract

Monolayers can be used as model membranes to investigate a variety of membrane specific interactions which regulate cell function such as hormone operation, immune response, etc. We have chosen to examine the binding of lectins to monolayers of lipopolysaccharides (LPS) as a model system for a number of other membrane specific recognition processes.

Lipopolysaccharides form the main component of the outer membrane of gram-negative bacteria and consist of a lipid component (called lipid A) covalently attached to a polysaccharide chain which can be subdivided into a core region and an O-antigen region. Lipid A consists of β 1-6 linked N acetyl glucosamine monosaccharide with between 4 and 8, but usually 6 alkyl chains. There is also a large degree of phosphate substitution which give the LPS a net negative charge. A group of mutant bacteria have been isolated which are deficient in the O-antigen component and synthesise only the core LPS. These are termed the rough (or R) mutant bacteria. The rough mutants are further subdivided according to the length of their polysaccharide chains.

Monolayers of rough mutant LPS were formed and characterised. Owing to their solubility in water the monolayers tended to slowly collapse when held at a constant surface pressure. However, injection of lectins (usually concanavilin A) into the subphase was found to arrest this collapse, the monolayers resist freezing such that no further collapse took place over a period of 18 hours.

In the pH range 5.5 to 7.0 concanavilin A exists as a tetramer with four binding sites for sugars. We believe that the protein cross-linked the LPS forming a rigid monolayer. This process could be reversed by injecting any of the sugars glucose, mannose, N-acetylglucosamine or fructose into the subphase, as these bind competitively with the conf.

MONOLAYER CHARACTERIZATION AND SURFACE ENHANCED RAMAN SPECTROSCOPY OF PHOTOSYSTEM II REACTION CENTERS

BP6

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The photosynthetic apparatus of higher plants consists of two separate, but linked, photosystems termed PS I and PS II. PS II is responsible for oxygen production arising from the splitting of water. The inherent lability and instability of PS II has greatly impeded progress in the elucidation of the details of its functioning but recent modifications of the preparative method have yielded significantly more stabilized samples.

PS II is of special interest in the context of molecular evolution because analysis of its peptide sequences indicate extended homologies with sequences of the much-studied photosynthetic bacterial reaction centers. The two systems have likely evolved from a common ancestral form. Monolayer studies of both systems are therefore in progress in an attempt to indicate functional and structural similarities. In addition, such monolayers have been characterized by surface enhanced resonance Raman spectroscopy (SERRS), which is capable of detecting submonolayer concentrations of suitable chromophores. SERRS is responsive to distance dependent conditions, i. e. the extent of displacement of a chromophore from the enhancing metal surface, so that inferences can be drawn regarding the location of these chromophores in a fixed membrane or monolayer.

PS II reaction centers consist of three major peptide units, D1, D2 and a cytochrome b-559; six chlorophylls; two pheophytins; two carotenes and one heme group. An additional peptide, CP47, is associated with the *in vivo* functionality. No detailed structure at the molecular level is yet available for this complex.

Monolayers were formed from PS II preparations which contained Tris buffer and dodecyl maltoside as a solubilizing agent. Surface isotherm determinations and monolayer transfer operations were carried out in a commercial circular trough. Monolayers were formed on roughened (electrochemically) silver surfaces for SERRS measurements. Monolayers were transferred by Langmuir-Blodgett dipping, Langmuir-Shaefer transfer (horizontal touching) and self-assembly (spontaneous adsorption). Surface isotherms were determined with variation of subphase pH and subphase temperature. The apparent areas per PS II unit clustered around 75 nm². This value can be compared to those found in a recent monolayer study of the reaction center of *Rps. viridis* (a photosynthetic bacterium); these ranged from 25 to 110 nm² per unit, depending upon the initial spreading density.

Data derived from SERRS spectra allow inferences to be drawn regarding positional and orientational states of the PS II complex in monolayer form. Reconstitution of PS II reaction centers with the CP47 unit apparently results in total occlusion or coverage of the cyt b-559; its characteristic peaks disappear. The mode of monolayer transfer had a marked effect on the resulting SERRS spectra. For self-assembled systems on Ag, strong carotenoid bands were evident, indicating a close proximity to the surface. LS and LB systems produced only weak carotenoid signals. Systems formed by LS transfer apparently had more material present on the Ag surface than those produced by LB transfer. LB-formed systems also had a higher background in their spectra.

Comparison of the SERRS spectra of the PS II reaction centers with preparations of reaction centers of photosynthetic bacteria indicate very marked similarities as regards peak positions and relative peak intensities. By these criteria the two systems appear quite closely related as regards their component composition.

DOMAIN STRUCTURE AND MOLECULAR CONFORMATION IN FILMS FROM FLUORESCENTLY LABELLED PHOSPHOLIPIDS

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Systematic investigations of DPPE-NBD (see inset of Fig. 1), DMPE-NBD and PC-NBD (fluorescence label in one of the tails) are performed both on monolayers at the air-water interface and deposited on solid substrates as Langmuir-Blodgett (LB) films. This dye compound is frequently used as fluorescent probe in fluorescence microscopy investigations of lipids in monomolecular layer films, model membranes, and living cell systems. It is also a suitable model compound for: charge transfer investigations, for understanding more complex molecules in LB films and for sensor applications.

We present first experimental evidence for the self-quenching of the fluorescence when higher-order "domains" of the dye are formed at the air-water interface (Fig. 2 a, b). For the first time a coexistence of the two completely different types of "domains" at the phase coexistence region for a single component system is observed (Fig. 2 a). From small-angle X-ray diffraction, pressure-area isotherms, molecular modeling, and polarized FTIR spectroscopy data molecular conformation as a function of surface pressure in the solid condensed region is estimated. The experimental data is related to the computer aided molecular conformational analysis of DPPE-NBD at the air-water interface (Fig. 3) and its mode of insertion into DPPC monolayer at the air-water interface (Fig. 4). This work was supported under contracts MU-NM-12 and F-19 with the Bulgarian National Science Foundation.

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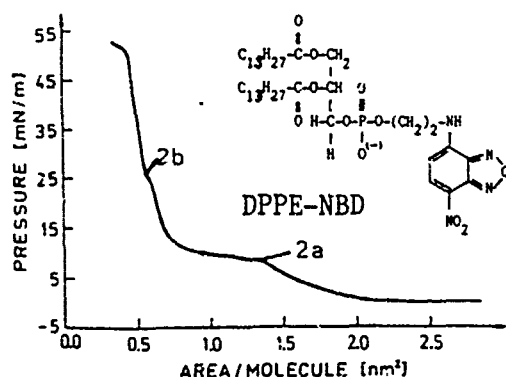


Fig. 1. Surface pressure-mean molecular area isotherm of DPPE-NBD at 20°C.

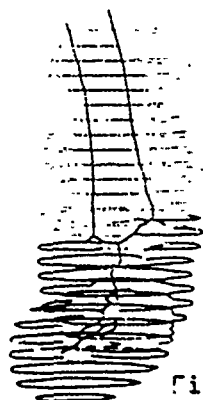
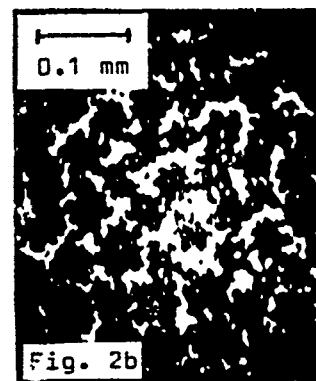


Fig. 3

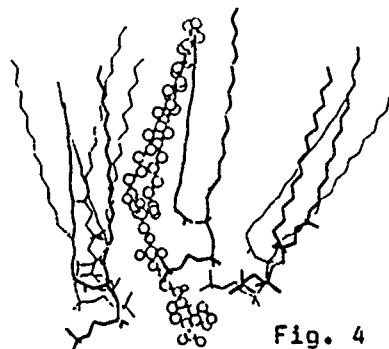


Fig. 4

PREPARATION OF LANGMUIR-BLODGETT FILMS FROM FLUORESCENTLY LABELLED PHOSPHOLIPIDS

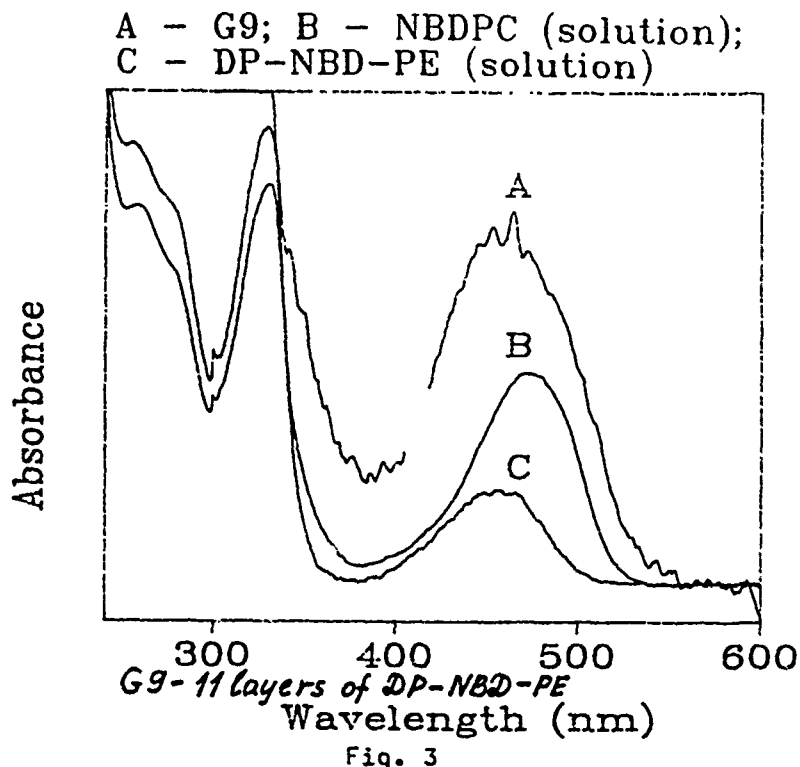
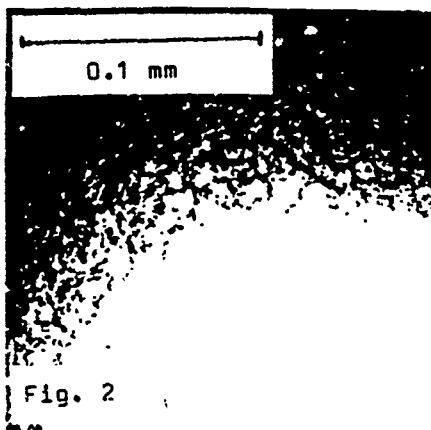
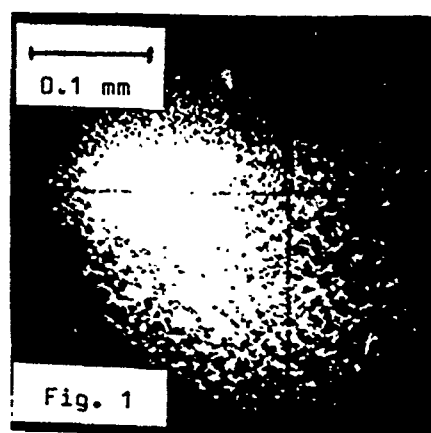
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For the first time Langmuir-Blodgett films from fluorescently head or tail labelled phospholipids are prepared (see previous poster). These substances are frequently used as staining dyes in fluorescence microscopy investigations of phospholipid films and vesicles. Its surface pressure - mean molecular area isotherms exhibit very rich polymorphism, partly explained by fluorescence microscopy observations (see BP7). Good quality deposition was possible on glass, quartz and sili-one wafers. Technological optimization and defect characterization by various microscopy techniques is performed. The phase coexistent structure (at 26 mN/m) is preserved during the transfer as observed by fluorescence microscopy (Fig. 1). Addition of bivalent ions leads to domain formation in multilayered LB structures as shown by dark field microscopy (Fig. 2). A novel method for drastically improving the film quality is suggested (Ref. 1). J-aggregation in the deposited films is observed (Fig. 3) which might be responsible for the fluorescence self-quenching in the condensed states (poster BP7). LB structures are characterized by small-angle X-ray diffraction, polarized UV-VIS and FTIR spectroscopy. This work was supported under contracts MU-NM-12 and F-19 with the National Science Foundation.

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GATING BEHAVIOUR OF PORIN CHANNELS IN MONTAL-MUELLER BILAYER MEMBRANES

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Abstract

The channel forming proteins known as porins are the main entry route for antibiotics through the outer membrane of bacterial cells. It is known that high transmembrane potentials ($> 80\text{mV}$) induce closure of these channels. Therefore, an understanding of this effect, known as voltage gating, is important not only in antibacterial research but may also provide an insight into the development of "switches" for molecular electronic applications. Accordingly, we have carried out a detailed study of the electrical characteristics of porin extracted from *Escherichia coli* and inserted into phospholipid bilayer membranes formed using the Montal-Mueller technique.

The current-voltage characteristics are found to be weakly asymmetrical, the degree of asymmetry decreasing with decreasing pH of the bathing medium. The direction of asymmetry reverses when the porin is incorporated from the opposite side of the bilayer, indicating that the protein inserts with a specific orientation. Increasing the pH of the bathing medium (i) increases the single channel conductance (ii) skews the histogram of insertion step sizes towards larger values and (iii) decreases the cation selectivity of the channel, providing evidence for the presence of fixed negative charges at or near the pore entrance.

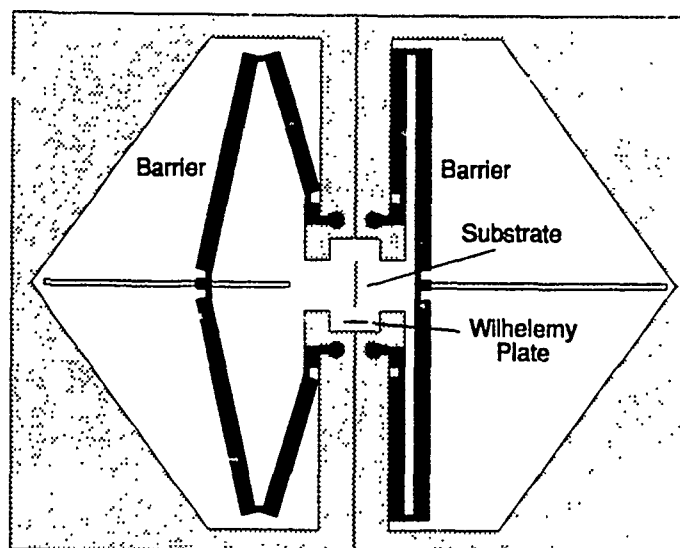
The gating behaviour of the channels has been studied with different applied voltages, temperatures and pH. Upon applying a sufficiently high voltage, the current through a bilayer incorporating a large number of proteins decays with time from its initial value. The dynamics of the decay suggest that a number of processes are occurring simultaneously.

A MODULAR TROUGH FOR LANGMUIR-BLODGETT DEPOSITION AND MONTAL-MUELLER BILAYER STUDIES

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A modular trough has been developed to facilitate Montal-Mueller studies of biomolecular membranes; it is a development of our earlier 'diamond' trough designs, and the Langmuir-Blodgett deposition facility is maintained. The basic structure is indicated below:



Each half of the trough is machined from a single block of PTFE, and incorporates a barrier with flexible regions (shown black) which is again made from a single piece of PTFE. When configured as shown, the trough acts as a symmetric LB trough; the surface area may be varied between 115 cm^2 and 17.5 cm^2 , and the subphase volume is about 550 cm^3 .

Flow diagrams have been determined; the shoulders formed by the main blocks channel the flow so that it is essentially normal to the surface of the substrate; this gives excellent films but may not be applicable to certain more rigid films.

The barriers are continuous, and in the Montal-Mueller mode it is possible to use the barriers to investigate surface film properties and set surface pressure before using external reservoirs to raise the water level and form the Montal-Mueller bilayer.

The totally modular structure leaves open other possibilities such as a deeper central dipping well or an alternating-layer arrangement based on a suitable central section.

IONIC SELECTIVITY OF VALINOMYCIN AND CROWN-ETHERS IN MONOLAYERS

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Macrocyclic ligands such as valinomycin and crown-ethers possess high membrane activity, including ability to selectively increase the cation permeability through both biological and synthetic membranes. The use of monolayer technique for model studies is suitable because provide simple membrane-like systems containing membrane-active molecules at known distances, concentrations and orientations with respect to the interface.

In present work the interaction of valinomycin and surface-active derivatives of various crown-ethers in monolayers with alkali metal cations from aqueous subphase was investigated.

It was shown the existence of two states of valinomycin in monolayers at the surface pressure lower and higher than 31.5 - 33.5 mN/m. The scheme describing the positions of valinomycin molecules at the interface was proposed. The influence of size of various anions on the stability of valinomycin-cation complexes at the interface was demonstrated.

The monolayer characteristics of surface-active derivatives of various crown-ethers as a function of nature and concentration of metal cations in the aqueous subphase, size of the polyether ring, number and dimensions of the hydrophobic long chains were analyzed. According to these data, the row of cation selectivity of crown-ethers at the interface was obtained. Prospects for applications of such systems as ionoselective membrane electrodes are discussed.

The authors are thankful to Dr. D. Möbius and coworkers (MPI of Biophysical Chemistry, Göttingen, FRG) for the possibility to measure the surface potential - molecular area isotherms for valinomycin and some crown-ethers.

P O S T E R S

SESSION C: SELF ASSEMBLY

Self-assembled monolayers of non-alkane thiols: the influence of intermolecular backbone interactions.

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To date, studies of self-assembled monolayers (SAMs) on gold surfaces have largely concentrated on investigating the properties of monolayers based on alkane thiols. In these films, intermolecular interactions between the adsorbed thiols consist of Van der Waals forces between the alkane chains, and headgroup interactions. We have investigated the monolayer-forming properties of thiol and disulfide molecules with backbone chains containing amide and ether groups. The presence of these groups should result in strong polar interactions between the chains and in steric effects, tending to reduce the close packing of the films.

The SAMs formed from these species have been analysed using a wide range of methods, including optical and electrochemical measurements. Contact angle and electrochemical measurements demonstrate that the monolayers are more disordered and less densely packed than those formed by equivalent alkane thiols and disulfides. SAMs can be formed by adsorption of the thiols and disulfides from a variety of solvents: the films thus formed show variation in their properties, apparently dependant on the polarity of the solvent.

Self-Assembled Organic Films On Gold

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Thiols and disulfides chemisorb spontaneously on gold surfaces and form self-assembled films. These ultrathin layers result in modification of the surface properties such as wettability, chemical reactivity and adhesion.

We synthesized the thiol $\text{HS-(CH}_2\text{)}_{11}\text{-OH}$ and the disulfide $[\text{-S-(CH}_2\text{)}_{11}\text{-OH}]_2$ and investigated their chemisorption on gold. For substrate preparation a gold layer of 100 nm was evaporated onto freshly cleaved mica which had been primed with an adhesion layer of 5 nm of chromium. The chemisorption was done by immersion of the gold substrate in a 10^{-4} M solution of the thiol or the disulfide in ethanol. After immersion the substrate was rinsed with solvent to remove excess material.

We studied the kinetics of the chemisorption within a time range from 15 minutes to 20 days by contact angle measurements (sessile drop). Within 15 minutes the contact angle dropped from 67° to 20° (thiol) or 36° (disulfide) indicating a fast chemisorption. In the case of the thiol the contact angle decreased further and reached a stable minimum at 10° after 52 h. The disulfide exhibited an unexpected behavior. Up to an immersion time of 22 h the contact angle decreased and reached a minimum of 25° . In contrast, after prolonged immersion (20 d) the contact angle increased and reached stable values between 52° and 62° . A possible explanation is to assume a partial removal of the chemisorbed disulfide film. To check this we took the same sample and put it in a freshly prepared disulfide solution for 22h. Nevertheless the contact angle remained high at 55° indicating no additional chemisorption of the disulfide.

We repeated the experiment and examined the chemisorbed disulfide layer by XPS. The amount of sulfur at the surface was 4.7% after 22 h (25°) and diminished to 2.5% after 20 d (53°). This can be rationalized either by a partial removal of the chemisorbed disulfide film or a reorientation of the monolayer film resulting in a better shielding of the sulfur by the methylene chain.

XPS studies of monolayers of the thiol on gold showed a reduction of the energy of the 2p electrons of sulfur of 1.9 eV (bulk: 163.4 eV ; monolayer: 161.5 eV). In the case of the disulfide the reduction was 1.4 eV (bulk: 163.1 eV ; monolayer: 161.7 eV). This proves that monolayer binding to the gold surface occurs by the formation of gold sulfide species $[\text{Au-S-(CH}_2\text{)}_{11}\text{-OH}]$.

SANDWICHED PROTEIN LAYERS: LAYER-BY-LAYER DEPOSITED MULTILAYER ASSEMBLIES OF STREPTAVIDIN AND BIOTINYLATED POLY-L-LYSINE

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INTRODUCTION

During the last three years we have developed a new method which allows to construct ultrathin multilayer assemblies by consecutive adsorption of anionic and cationic polyelectrolytes out of aqueous solution [1-4]. The technique allows the preparation of multicomponent films that can be deposited on surfaces with any given topology. They show excellent thermal stability and the average film thickness can be adjusted to within a few Ångströms.

RESULTS AND DISCUSSION

Films are deposited in a layer-by-layer fashion, thus enabling the construction of multilayers with complex architectures by incorporating different functionalities in different layers. Here we report on the assembly of multilayers in which streptavidin is sandwiched between layers of biotinylated poly-L-lysine. Fig. 1 demonstrates the regular buildup of the films as monitored by small angle X-ray reflectivity.

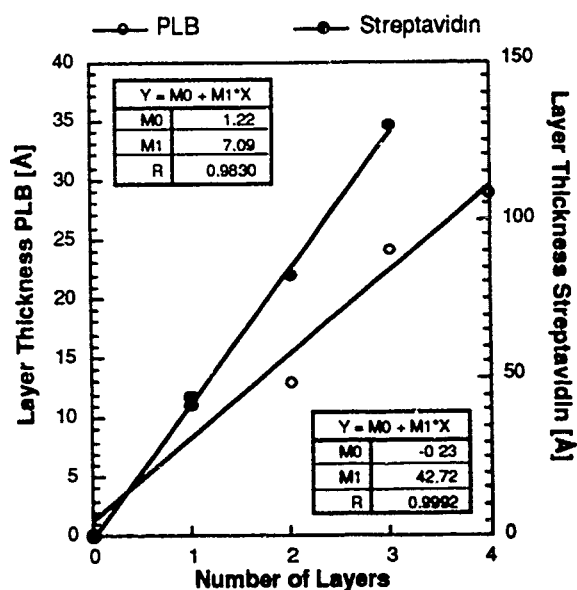


Figure 1: Linear increase of the accumulated film thickness of the streptavidin and biotinylated poly-L-lysine layers (PLB) on a precursor film of polystyrenesulfonate and polyallylamine on a float-glass substrate.

Fig. 1 shows the adsorption of three layers of streptavidin deposited in a sandwiched assembly. A thickness was measured per layer of protein, which is in excellent agreement with the dimensions of the protein. The fact that alternating protein/polymer films can be

assembled proves two facts: 1) some of the four binding pockets of the protein remain active and solution-exposed after adsorption and 2) multilayer buildup is not only possible by electrostatic attraction but also by biospecific recognition.

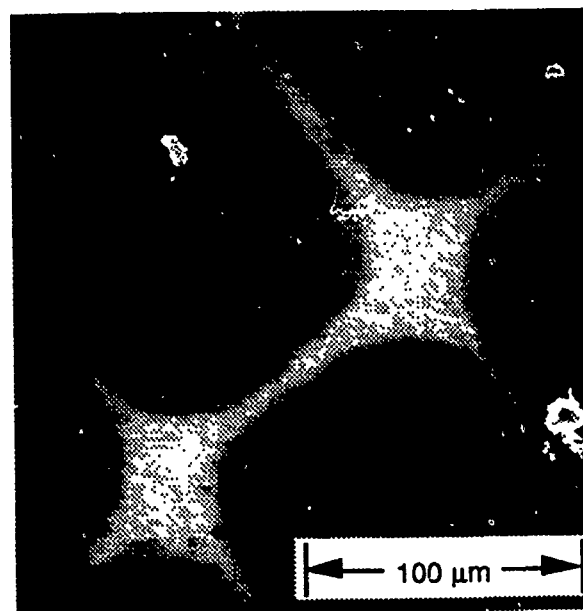


Figure 2: Fluorescence micrograph of FITC-labelled streptavidin monolayer specifically adsorbed to a laterally photostructured precursor film. Dark areas represent photodesorbed film, bright areas correspond to the intact biotinylated surface, a prerequisite for streptavidin binding.

Layer-by-layer deposited films of polyelectrolytes can laterally be photostructured by UV-irradiation (Fig. 2) in a similar way as already reported in Ref. [5] for octadecyltrichlorosilane monolayers on silicon oxide surfaces.

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**Self-Assembled Multilayers of ω -mercaptoalkanoic Acids:
Effect of Incorporating Bulky Polar Groups**

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The technique of self assembly provides a route for the formation of systems ordered at the molecular level. This poster reports on the formation of multilayer films using selective ionic interactions. A self-assembled monolayer is formed, from alkanethiol molecules functionalised with an acid head group; to provide a carboxylic acid surface. A suitable metal salt can be formed on this surface - and then to this, one can chemisorb a second alkanethiol monolayer. Repeating the procedure, of salt formation and alkanethiol adsorption, facilitates the build up of multilayer structures.

A variety of techniques have been used to study the formation of multilayers of the ω -mercaptoalkanoic acid $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ in an attempt to clarify the principles underlying the formation of such assemblies including ellipsometry, wetting, FTIR spectroscopy and XPS.

The ability to incorporate chromophores into such multilayer forming molecules is of particular interest due to the intrinsically non-centrosymmetric nature of the films produced which is of interest for a variety of technological applications from non-linear optical to piezo and pyro-electric effects.

We have made preliminary studies of film formation of molecules containing chromophores, in particular, $\text{HS}(\text{CH}_2)_{11}\text{-O-C}_6\text{H}_4\text{-SO}_2(\text{CH}_2)_5\text{COOH}$, and present FTIR spectroscopy results detailing the film formation process.

Our results show that it is possible to build up multilayers via selective ion interactions and that the introduction of a chromophore group does not prevent regular formation of multilayer assemblies.

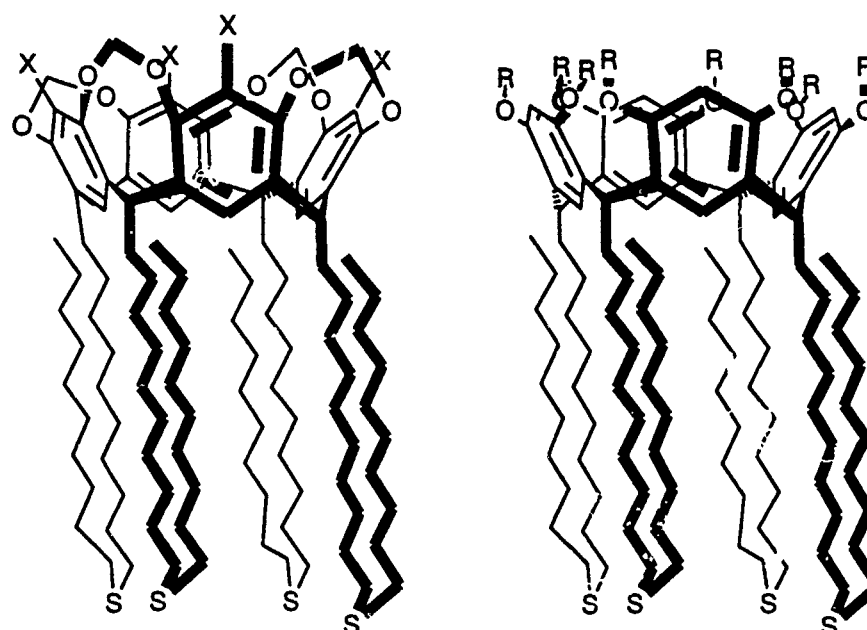
* To whom correspondence should be addressed

SELF ASSEMBLED MONOLAYERS OF HOST MOLECULES ON GOLD

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Adsorbates with four sulphide side chains and a small rigid cavity can be made reasonably easily using commercial available starting compounds.



$X = \text{H}, \text{CH}_3, \text{Br}, \text{CN}, \text{CC-OEt}$

$R = \text{H}, \text{CH}_3, \text{CO-CH}_3$

When a freshly evaporated polycrystalline gold mirror is immersed in a diluted solution of these adsorbates, its surface properties are completely changed. The surface becomes hydro- and oleophobic and its ability to suppress the oxidation and rereduction of a 1 mM solution of $\text{K}_4\text{Fe}(\text{CN})_6$ is only slightly worse than that of a dodecylthiol monolayer.

SPR thickness measurements reveal that a layer has grown onto the gold which is only slightly less thick than expected for a monolayer. Moreover AFM shows that the surface structure is ordered and different compared to uncovered gold. First attempts to make Polarized Infrared External Reflectance spectra of these covered gold mirrors were partly successful; the presence of some adsorbates on gold could be confirmed.

Collaboration with several European surface analytical groups to determine the surface structures better is on going; XPS, static-SIMS and PIERS will be used in the near future.

POSTERS

SESSION D: SUPERMOLECULAR STRUCTURES

ALTERNATE LAYER LB FILMS CONTAINING POLYSILOXANE MONOLAYERS

W.H.A. Majid and T. Richardson

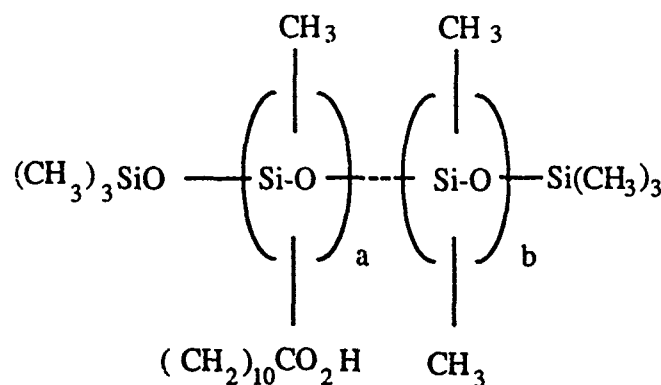
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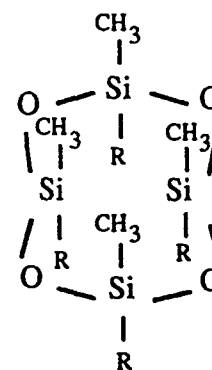
S. Holder and D. Lacey

Department of Chemistry, University of Hull, Hull (U.K).

Alternate layer LB films containing a range of polysiloxane monolayers co-deposited with a monomeric compound have been investigated. Several such systems have been shown to exhibit the pyroelectric effect. FTIR spectroscopy has been used, amongst other techniques, to relate the ionised state of the molecule to the pyroelectric response. Examples of linear and cyclic polysiloxanes molecules substituted with aliphatic pendant side-group are shown in the figure below. The isotherms of these molecules suggested that the average area per each silicon unit is around 0.2 nm^2 which confirms that the Langmuir films are indeed monomolecular. A number of different aliphatic acid chains have been substituted onto the backbone / ring and the effect on the Π -A isotherm and the pyroelectric activity has been studied. It is found that the pyroelectric activity of linear polysiloxanes increases as the length of the aliphatic acid chain decreases.



Linear Polysiloxane : $a = 7, b = 6$.



Cyclic Polysiloxane : $R = (\text{CH}_2)_{10} \text{CO}_2 \text{H}$

ELECTROPOLYMERISATION of SUBSTITUTED FURANS and THIOPHENES LEADING to CONDUCTING FILMS

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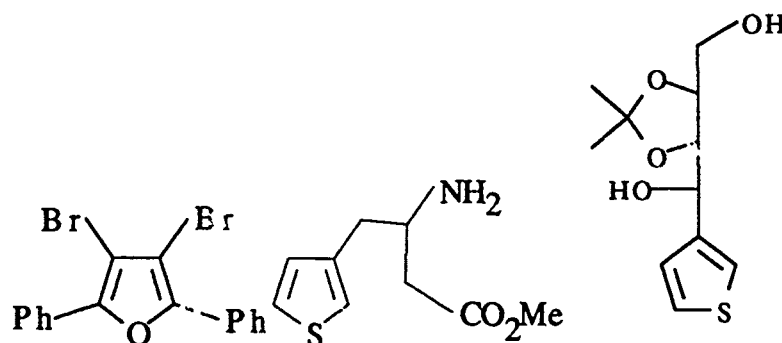
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Polymerisation of the thiophene and furan nuclei to provide thin films has been extensively studied.¹ The usual route to these systems can involve either electropolymerisation or the polymers can be obtained by transition metal catalysed processes.² The latter route, although allowing access to gram quantities of the requisite polymers has associated with some inherent problems, the major ones being reproducibility and difficulty in controlling the molecular weight of the polymer produced.

Studies with substituted thiophenes have generally concentrated on having alkyl or aryl substituents at the three position of the heterocyclic ring. The rationale for this approach has been that the 2-position of the ring system has a lower oxidation potential value than the 3 or 4 positions of the substituted ring systems.

Herein we report that electrochemical polymerisation can be successfully employed, with monomers having functional groups in their side chains, to produce thin films. This has resulted in the synthesis of a chiral, conducting thin film.



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STRUCTURE, MORPHOLOGY AND PHASE TRANSITIONS IN FREELY-SUSPENDED, TRANSFERRED FREELY-SUSPENDED AND LB-FILMS OF LIQUID-CRYSTALLINE N-ALKYL-4'-N-ALKOXYBIPHENYL-4-CARBOXYLATES

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INTRODUCTION

N-Alkyl-4'-n-alkoxybiphenyl-4-carboxylates possess both amphiphilic and liquid-crystalline properties. This combination of two driving forces for the supramolecular aggregation allows the preparation of ultrathin multilayered films on solid substrates by two different methods: the Langmuir-Blodgett (LB) technique and the technique of transferring freely-suspended (FS) films/1/.

RESULTS AND DISCUSSION

The remarkable similarity of the structures of the transferred freely-suspended (TFS) and LB-films, perpendicular to the substrate surface, is shown by small angle X-ray scattering/2/. Nevertheless both types of multilayer assemblies, prepared from the same substance (ethyl-4'-n-octyloxybiphenyl-4-carboxylate), show a different thermal behavior (Fig. 1).

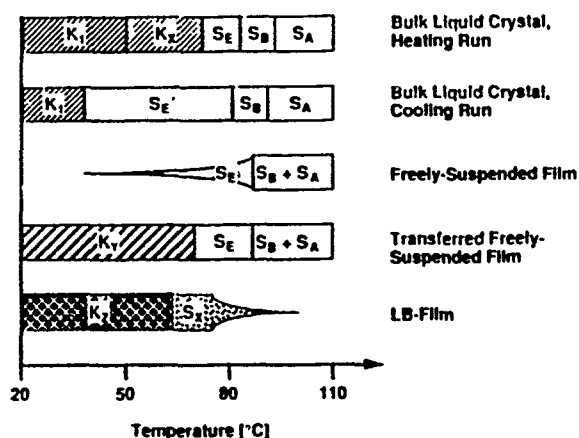


Figure 1: Thermal behavior of the different multilayer assemblies of ethyl-4'-n-octyloxybiphenyl-4-carboxylate. Whereas the TFS-films undergo reversible phase transitions and are stable up to the clearing point of the bulk material (110 °C), the LB-films show only one irreversible phase transition and start to melt already 30 °C below the clearing point of the bulk material.

The assumption that these temperature dependencies are due to different defect types and densities in both kinds of films could be corroborated by atomic force

microscopy (AFM) (Fig. 2)/3/. For this purpose the best film forming compounds were used: ethyl-4'-n-octyloxybiphenyl-4-carboxylate for the TFS-films and methyl-4'-n-heptyloxybiphenyl-4-carboxylate for the LB-films/4/. The bilayer holes that are prominent in LB-films are missing in TFS-films. However, the cracks in the crystalline phase of the TFS-films, that probably arise from cooling the film on the solid substrate, are not observed in LB-films, because they do not even survive heating above the S_X -phase.

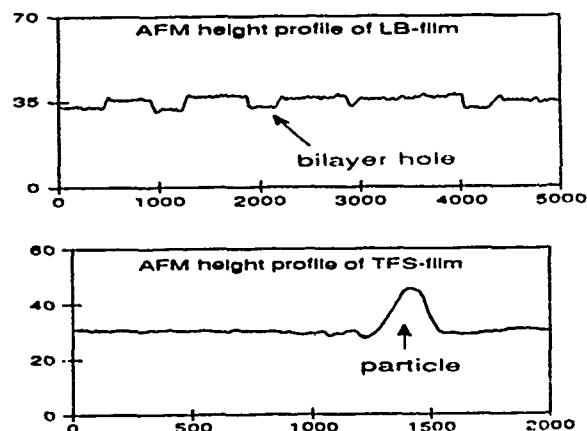


Figure 2: Side-views of AFM height profiles of a LB-film (top) and a TFS-film (bottom). The cross-cut of the LB-film shows holes with a step size corresponding to exactly one bilayer. The TFS-films possess molecularly flat planes. The rise in the profile corresponds to a random feature (particle).

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LAYER-BY-LAYER DEPOSITED SUPRAMOLECULAR FILM ASSEMBLIES OF ANIONIC AND CATIONIC POLYELECTROLYTES: AN X-RAY STUDY OF THE THERMAL BEHAVIOUR AND THE EFFECTS OF ADDED SALT.

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INTRODUCTION

During the last three years we have developed a new technique which allows to construct ultrathin multilayer assemblies by consecutive adsorption of anionic and cationic polyelectrolytes out of aqueous solution^{1-5/}. The principle of this layer-by-layer adsorption is schematically depicted in Fig. 1. Our method allows the fabrication of functional multicomponent films that can be deposited on surfaces with any given topology. They show excellent thermal stability and the total film thickness can be adjusted to within a few Ångströms.

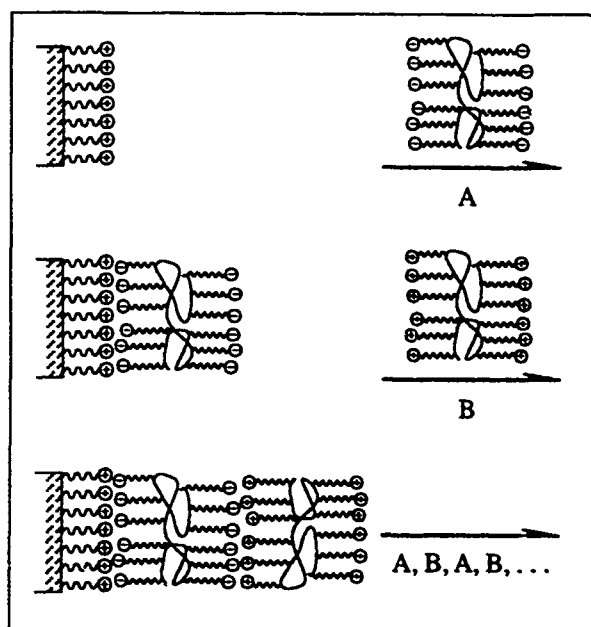


Figure 1: Side-view schematic depicting the consecutive adsorption of polyelectrolytes (polymer structures are highly idealized). A positively charged substrate is immersed in the solution containing the anionic polyelectrolyte and a monolayer of the polyanion is adsorbed (step A). After rinsing, the substrate is immersed in the solution containing the polycation, again, a monolayer of the cationic polyelectrolyte is adsorbed, thereby restoring the original surface charge (step B). Cyclic repetition of both steps (A, B, A, B, ...) yields alternating multilayer assemblies of both polymers.

RESULTS AND DISCUSSION

Here we report on the influence of added electrolyte on the adsorption of the polyelectrolytes. The influence of salt on the conformation of polyelectrolytes in solution

is well established. By adsorbing the polymers onto a flat surface, the thickness of the polymer layers is easily and precisely accessible by X-ray reflectivity. We have investigated the influence of different concentrations of MnCl_2 and NaCl on the thickness of adsorbed polystyrenesulfonate. As expected, the film thickness grows with increasing electrolyte concentration. Due to the better screening of the electrostatic repulsion by the bivalent Mn^{2+} , its effect on the conformation of the polymer is more pronounced. A typical reflectivity curve is shown in Fig. 2

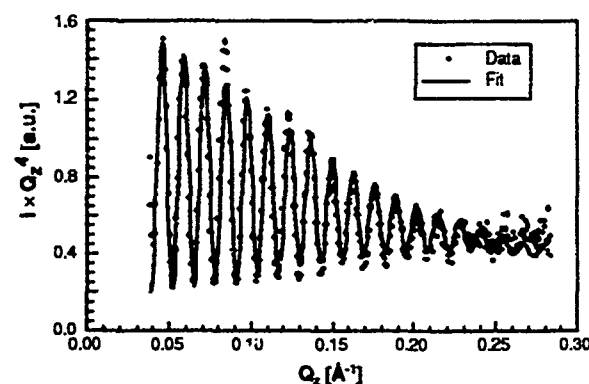


Figure 2: X-ray reflectivity curve of a 56 layer film of sodium polystyrenesulfonate and polyallylamine hydrochloride taken at 150°C. The full circles represent the data points and the solid line the corresponding fit. From the numeric fit one obtains the film thickness and an estimate for the roughness of the film surface.

The films are stable up to at least 190°C, but their thickness is dependent on temperature. The film whose reflectivity curve is shown in Fig. 2 has a thickness of 596 Å at ambient temperature which is reduced to 504 Å at 150°C. Above this temperature bound water is lost as additionally verified by FTIR-spectroscopy.

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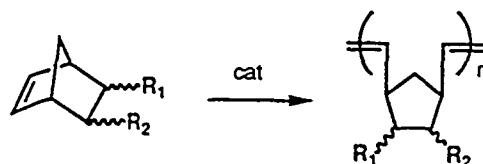
Spreading Behaviour of Norbornene Monomers and Polymers

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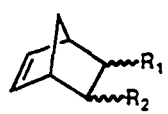
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In recent years, functionalized amphiphilic polymers have been used advantageously for the preparation of polymeric monolayers and multilayers, due to the improved stability¹⁾. Unfortunately, many chemical functional groups, such as the nitro-group -NO₂, are not, or only barely, compatible with most polymerization methods. Such polymers however would be most useful for a number of purposes, e.g. non-linear optical (NLO) applications.

Stimulated by the recent progress in ring opening metathesis polymerization (ROMP)^{2,3)}, we have investigated the polymerizability of amphiphilic, functionalized norbornene monomers, using a catalyst based on RuCl₃*H₂O. This catalyst is easily prepared and stable in air as well as in aqueous environment, thus enabling facile polymerization procedures.



The spreading behaviour of the various monomers and polymers prepared was studied with respect to their molecular architecture. Although the rather bulky norbornene group may interfere with the self-organization of the compounds, well-defined monolayers can be produced choosing appropriate structures of the amphiphiles.

e.g.	R ₁	R ₂
		
	-COO-(CH ₂) ₁₅ -CH ₃	
	-COOH	-COO-(CH ₂) ₁₅ -CH ₃
	-H	
	-H	-COO-(CH ₂) ₁₁ -O-C ₆ H ₄ -CH=N-NH-C ₆ H ₄ -NO ₂

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KINETICS OF POLYMERIZATION OF THE ACRYLIC AND DIACETYLENE LIPID-LIKE MONOMERS IN MONOLAYERS

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The polymerization of surface-active monomers in monolayers at the gas/liquid interfaces is the unique method for preparation of highly stable oriented membranes, which can serve as model systems for investigation of biological membranes and also as promising materials for advanced nanotechnology.

The lipid-like monomers with different position of the polymerizable group in hydrophilic and hydrophobic part of molecule: N-acryloylphosphatidylethanolamine (ACPE) and 1,2-di-O-tetracosyl-11,13-diinoylglycerol-3-phosphorylcholine (DTPC) were synthesized. The surface-active properties and kinetics of polymerization of these monomers in monolayers at UV-irradiation (254 nm) were investigated.

The studied monomers exhibit two states in monolayers (liquid-expanded and liquid-condensed), which are more pronounced in the case of DTPC and initial tetracosyl-11,13-diinoic acid (TDA). The rate of polymerization of these diacetylene monomers is close to zero at low surface pressures ($< 0.5 \text{ mN/m}$), because of the topochemical character of this reaction. The rates of polymerization of DTPC and TDA rapidly increase with increase of the surface pressure (maximum values at 8 and 12 mN/m , respectively) and decrease with further increase of surface pressure (rapidly - until 20 mN/m) that correlate with differences in orientation of these molecules in monolayers.

The rate of polymerization of ACPE rapidly decreases with small increase of the surface pressure (from 2 to 5 mN/m), slightly increases in the range of 5 - 14 mN/m and slowly decreases at higher pressures. The opposite character of the kinetics of polymerization for DTPC and ACPE at low surface pressures is explained by different nature and position of the polymerizable groups in hydrophobic and hydrophilic part of the molecules.

POSTERS

SESSION E: SENSORS

Vapour Sensing using a Polypyrrole Film coated AT-crystal

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The vapour sensing properties of electropolymerised polypyrrole tetrafluoroborate films were investigated as a coating on an AT-cut crystal, operating in the differential mode, versus an untreated reference crystal (see Fig. 1).

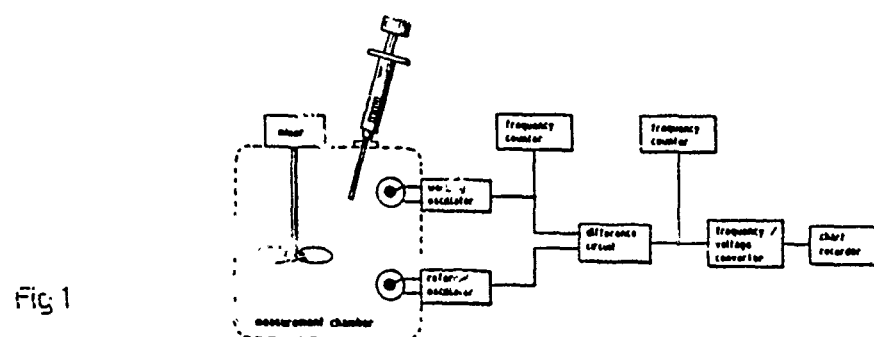


Fig 1

Electropolymerised polypyrrole films were shown to have a porous open structure when visualised by SEM making them ideal for vapour sensing applications. The best quality polypyrrole films were obtained by electrodeposition from a non-aqueous solvent. A clear difference in response was observed on exposure of these coatings to polar or nonpolar solvent vapours. Polar solvents caused a decrease in crystal frequency ($-\Delta F$) (see Fig. 2) whilst non-polar solvents caused an increase in frequency ($+\Delta F$) (see Fig. 3), versus a reference uncoated crystal. This difference in frequency is rationalised on the basis that polar solvents alter the viscoelastic properties of the polypyrrole film by making it more fluid whilst non-polar solvents have the opposite effect and make the film stiffer.

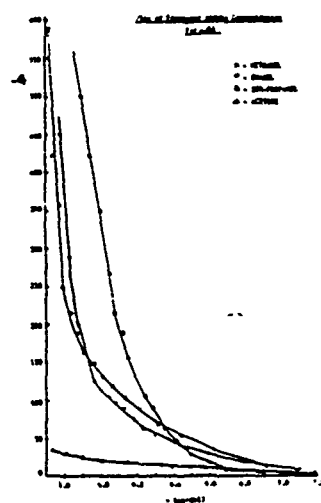


Fig. 2

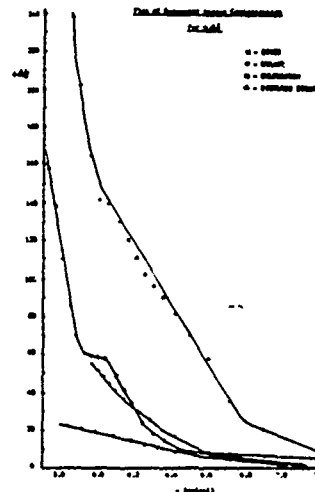


Fig. 3

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HIGHLY SPECIFIC SPR IMMUNOSENSOR BASED ON STREPTAVIDIN/BIOTIN TECHNOLOGY

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Abstract

Surface plasmon resonance spectroscopy (SPR) is a technique for measuring the thickness and complex refractive index of thin films. When the thin film is a layer of antibodies then the technique can be used as an immunosensor. Generally, immobilization of the sensing layer onto the solid surface is achieved by physical adsorption. However, this approach has serious drawbacks such as denaturation of the protein layer in contact with the metal, non-specific adsorption of proteins and ineffective coupling of the base layer to the metal.

We have overcome these problems by constructing a specific antibody/antigen sensor in which a base layer of streptavidin is immobilised onto a solid surface using biotin. A biotinylated antibody is then immobilised to this highly orientated monolayer of streptavidin to form the final sensor.

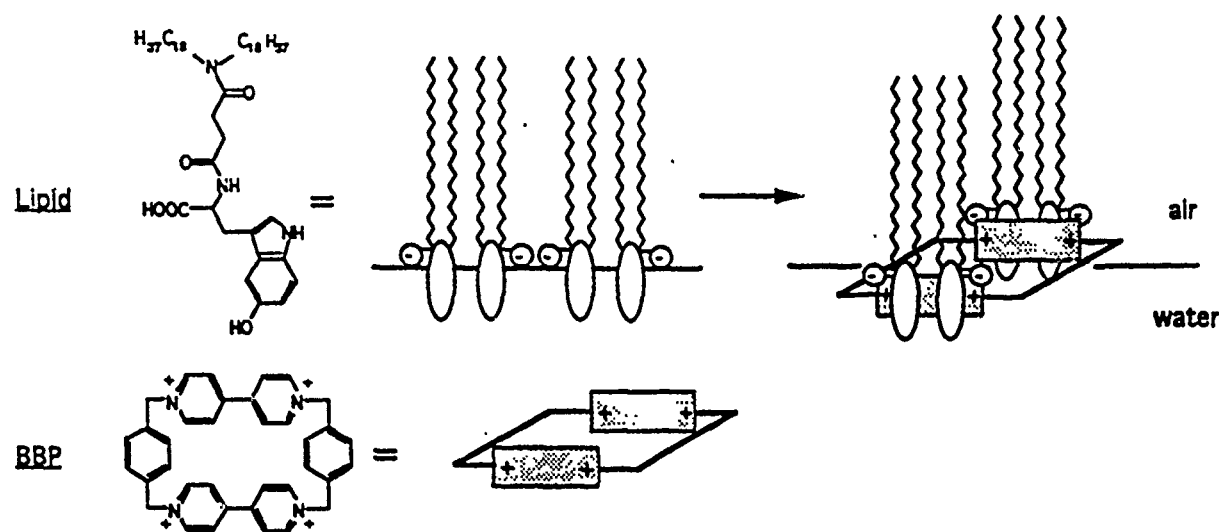
As an example, we have constructed a sensor for sex hormone binding globulin (SHBG) using the biotinylated antibody to SHBG. Coverage of the metal with antibody is over 50% (greater than other literature values) and stability to chemical agents is excellent. Using SPR to monitor the binding of the antigen to the antibody allows the detection of subnanomolar concentrations of the antigen in human serum (from a third trimester pregnancy). The kinetics of binding are consistent with the Langmuir isotherm giving $K = 2.5 \times 10^7 \text{ M}^{-1}$ compared with $K = 1 \times 10^7 \text{ M}^{-1}$ as determined by immuno-radiological techniques.

Interactions involving hydroxytryptophan-, dihydroxynaphthalene-lipids, DMPA and
cyclobis(paraquat-p-phenylene) at the air-water interface

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The interaction of cyclobis(paraquat-p-phenylene) (BBP) and lipids with ionic and/or electron donor functions (dihydroxynaphthalene-, hydroxytryptophan-lipids and DMPA) were investigated. Both the adsorption technique and the cospreading technique were used to produce BBP containing monolayers. They were characterized by isotherm measurements, surface potential-area isotherms, UV-reflection- and fluorescence spectroscopy.

BBP is a rigid host molecule with a cavity capable to form CT-complexes with electron donor compounds as guest molecules. The rigidity and symmetry of BBP is interesting for basic investigations of formation and arrangement processes at ionic monolayers. Its ability to act as a host allows to investigate the specific interaction with guest lipids in the monolayer or with water soluble guests coming from the subphase. It is shown that the pure ionic interaction (with DMPA or RCOOH) leads to defined BBP monolayers depending on the dissociation rate of the ionic group and the amount of BBP used in the experiments. The bare CT-interaction between the dihydroxynaphthalene-lipid and BBP, however, is not strong enough to fix the BBP at the surface. The combination of both types of interactions (hydroxytryptophan-lipid) may lead to BBP monolayers with CT-complexes at the air-water interface.



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P O S T E R S

SESSION F: MOLECULAR ELECTRONICS

RUBBED LB-FILMS USED AS COUPLING-LAYERS FOR SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTAL DISPLAYS

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Handling of Polyimide-Langmuir-Blodgett (PI-LB) alignment layers for surface stabilized ferroelectric liquid crystal (SSFLCs) cells is investigated and optimized. Different kinds of indium tin oxide (ITO) substrates were compared relating to surface roughness and structure by scanning tunnelling microscopy. The decrease of surface corrugation by deposition of a single PB-LB layer is shown. The orientation of the layers was measured by optical retardation. Small substrates (width up to 5 mm) showed spontaneous orientation due to the deposition process, whereas at bigger probes additionally rubbing was necessary. The order parameter for LB Layers induced by rubbing was calculated. The perfect alignment properties can be seen in bistable high contrast SSFLC matrix cells.

QUANTUM CHEMICAL INVESTIGATIONS OF THE PHOTOACTIVE CHARGE
TRANSFER SUPERMOLECULES, SUPRAMOLECULES AND DESIGN OF THE
MOLECULAR DEVICES

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Quantum chemical investigations of the organic photodonor, photoacceptor and insulator molecules as well as its single ions were performed by using MNDO and molecular fragmentation method [1]. It was calculated such a photodonor molecules: Carbazole (Cz), Dimethyl-phenyl-diamine, photoacceptor molecules: 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 7,7,8,8/tetracyanoquinodimethane, 2,4,7-trinitro-9-dicyano-fluorene, 2,4,5,7-tetranitro-9-dicyano-fluorene, 1,2,4,5-tetracyanobenzene, 2,3-dichloro-5,6-dicyanobenzoquinone, tetrafluoro-7,7,8,8/tetracyanoquinodimethane as well as the insulator molecules: C_2H_6 , C_3H_8 , C_5H_{12} .

It was found the most active atoms in the above named molecules and design as well as quantum chemical calculations of the Cz-insulator-photoacceptor supermolecules, Cz::photoacceptor supramolecules was done.

The localization of the additional electron hole in the Cz and additional electron in the acceptor molecules has been found. We offer to use these local charge distribution regions in the construction of the basic elements of the radiation solar energy cells as well as of the molecular computers.

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CHARACTERISATION OF LB FILMS OF MONO- AND DI-VALENT SALTS OF
DIDODECYLDIMETHYLAMMONIUM-METAL(DMIT)₂

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Abstract

LB films formed from mono- and di-valent salts of the charge transfer complex didodecyldimethylammonium-M(dmit)₂, where M = Ni, Pt or Pd, have been deposited by vertical dipping. The higher dimensionality of these complexes should lead to films with higher conductivity than hitherto observed with 1-d complexes which are prone to stacking defects. We show here that the pressure-area (π -A) isotherms of dmit salts and the quality of the deposited film are very dependent on the time allowed for the complex to spread at the air-water interface prior to compression and subsequent deposition.

Within a few minutes of spreading at the air-water interface, the surface potential, ΔV , of the monolayer rises to 320 mV but then decreases slowly. Given a sufficiently large spreading area the potential decreases to zero indicating that the gaseous phase has been achieved. Depending on the volume and concentration of the spreading solution, this may take from 30 minutes to several hours. The effect of spreading time on the π -A isotherm is especially marked for the monovalent salt but is also significant for the divalent salts.

Phase contrast microscopy and ΔV measurements on deposited LB films show a much more uniform structure when long spreading times are employed. The conductivities of doped LB films prepared from poorly-spread monolayers are higher than those prepared from well-spread monolayers because of the presence of thicker, polycrystalline regions in the former. Consequently, the conductivities reported to date for LB films of dmit salts are likely to be significantly overestimated because of poor film quality.

POSTERS

SESSION G: NON-LINEAR OPTICS

Noncentrosymmetric Langmuir-Blodgett Multilayers for Second Harmonic Generation

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For the application of LB films in second order nonlinear optical devices such as frequency doublers, modulators or parametric amplifiers the high $\chi^{(2)}$ values reported from LB monolayers /1/ must be transferred to multilayers. To reach noncentrosymmetric multilayer structures alternate layers from NLO-active and inactive material must be prepared by a so called AB-trough.

For the preparation of alternating multilayers a so called "continuous AB through" was developed. Continuous in this sense means that the monolayers were prepared continuously at the air-water interface in a water flow channel /2/. In such a system the molecules are spread from solution onto a laminar water stream and are compressed by the stagnation of the surface water flow. For the alternating layer deposition a system containing two flow channels was set up. In comparison to conventional AB-troughs the flow channel system used in this work allows a more efficient deposition of alternating films to solid substrates.

AB-films from the active phenylhydrazon and several inactive monomeric and polymeric partners up to 50 bilayers were produced. The alternating films were characterised by SHG with a Nd-Yag laser. As would be expected in films which maintain a high degree of order independent of film thickness the second harmonic intensity increased quadratically with the number of dye layers and $\chi^{(2)}$ was independent from film thickness. The value of $\chi^{(2)}$ was strongly dependent on the choice of material for the buffer layer; for the best system a value of $\chi^{(2)} = 20 \text{ pm/V}$ at 1064 nm was obtained.

For comparison alternating films up to 30 bilayers were prepared with a conventional AB trough from KSV. In the SHG-measurements no significant difference to the films prepared by the flow channel system was observed.

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GP 2 Second Harmonic Generation from LB Mono- and Multilayers of Poly(isocyanide)s.

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Abstract:

In this study poly(isocyanide)s, fig. 1, with azobenzene based side chains, are used for Langmuir-Blodgett film formation.

These rigid-rod helical polymers can be obtained either racemic or optical pure.

The polymers 2-5 are not forming stable layers probably because lack of hydrophilicity. Preparing poly(isocyanide)s with an ester function (6) at the end of the large substituent or a spacer (7) should overcome this problem. Nevertheless these polymers form stable layers upon mixing them with amylose-ester derivatives. The mixed monolayers deposited well, Y-type, on different kinds of substrates, with constant transmittances. Monolayer thicknesses and refractive indices were measured by means of ellipsometry. These showed to scale linear with the fraction poly(isocyanide).

Second Harmonic Generation from multilayers was enhanced in case of using a polymer obtained by polymerizing an optical pure isocyanide (3 vs 4).

Preliminary measurement on floating monolayers showed also S.H.G. in case of the racemic poly(isocyanide) (3).

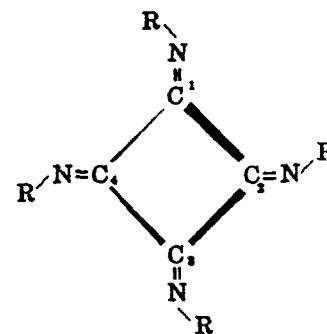


Figure 1: Structure of a poly(isocyanide). C5 is behind C1 etc.

Polymer	configuration at C [*]	R in $\left[\begin{array}{c} \text{C}=\text{N}-\text{CH}-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{R} \\ \\ \text{CH}_3 \end{array} \right]_n$
1	(S)	$-\text{CH}_3$
2	(R,S)	$\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$
3	(R,S)	$\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}((\text{CH}_2)_3\text{CH}_3)_2$
4	(S)	$\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}((\text{CH}_2)_3\text{CH}_3)_2$
5	(S)	$\text{NO}_2-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}((\text{CH}_2)_3\text{CH}_3)_2$
6	(S)	$\text{NO}_2-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}((\text{CH}_2)_2\text{O}-\text{C}(=\text{O})-\text{CH}_3)_2$
7	(R,S)	$-(\text{CH}_2)_{10}-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{NO}_2-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}((\text{CH}_2)_3\text{CH}_3)_2$

Phase-Matched Frequency-Doubling in Langmuir-Blodgett Film Waveguides

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We report phase matched second harmonic light generation by mode conversion obtained for the first time with a nonlinear optically active LB film. We convert a fundamental TE_0 mode into a second harmonic TE_1 mode using a four layer optical waveguide geometry: a substrate (fused silica), a linear optical waveguide (SiO_2/TiO_2), the nonlinear optically active LB film (2-docosylamino-5-nitropyridine, DCANP) and air as cover. For DCANP this configuration improves the theoretical conversion efficiency by a factor of more than 100 compared to a conventional three layer geometry (substrate-DCANP-air). The reason for this improvement is that the overlap integral in the four layer geometry is much larger than in the three layer configuration.

The DCANP LB films have an inplane overall polarization. The advantage of using such a material is pointed out. The experiments are carried out with a pulsed Ti:Sapphire laser. Gratings are used to couple the light into the waveguide. Guided wave attenuation coefficients of $\alpha = 5.5 \pm 0.5$ dB/cm are measured for the fundamental mode at the wavelength of $\lambda = 926$ nm. Conversion efficiencies of $\eta = P(2\omega)/P(\omega) = 0.6$ % are obtained ($P(\omega)$ inside the film). The calculated and measured efficiencies agree reasonably. Possibilities for further improvements are discussed.

Recently we have also demonstrated Cerenkov-type phase matching for the first time with LB films (Bosshard, Flörsheimer, Küpfer, Günter, *Opt. Commun.* **85**, 1991, 247) where only the fundamental beam is guided and the second harmonic is radiated into the substrate. We now compare the advantages and disadvantages of both types of phase matching.

Aminonitrostilbene Carboxylic Acid LB Films for Electrooptics

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Abstract

A series of four aminonitrostilbene carboxylic acids and one aminonitrostilbene methyl ester is assessed for LB deposition and the Pockels effect.

The materials contained a range of different length of alkyl chains (attached to the nitrogen of the amine group) and also varied in the length of the carboxylic acid. These modifications were found to have a marked effect on the behaviour of the floating monolayer. For short chain lengths the films were extremely rigid and could not be transferred to a substrate. As the length was increased the films became progressively less rigid and the surface area per molecule was observed to increase.

The least rigid material (1-40A) was deposited onto a silver substrate as a mixed monolayer with 22-tricosenoic acid. This film was then characterised for the Pockels effect at 633 nm wavelength using an attenuated total reflection arrangement. The measured response was $\chi^{(2)}(-\omega; \omega, 0) = 143 \text{ pm V}^{-1}$ one of the largest values obtained for an LB film.

CHEMICAL AND PHOTOCHEMICAL PROPERTIES OF "GEDYE" MEROCYANINE LANGMUIR-BLODGETT FILMS

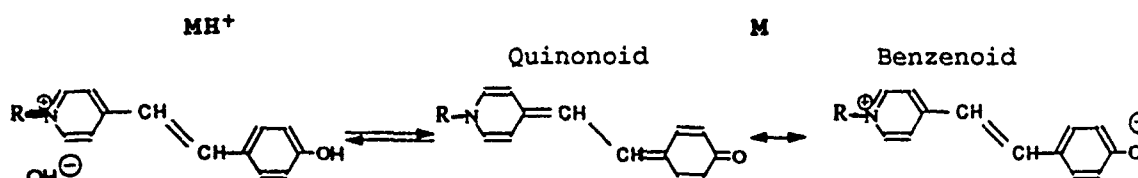
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The amphiphilic "gedye" merocyanine, 1-octadecyl-4-((oxocyclohexadienyldiene)ethylidene)-1,4-dihydropyridine, is known for its large hyperpolarizability, one of the necessary properties for the second harmonic generation (SHG). This merocyanine can exist in a protonated form (MH^+) and a base form (M) with a quinonoid and a benzenoid limit formulas. Due to an intra molecular charge transfer the last configuration is responsible of the hyperpolarizability and solvatochromism properties. In protic medium, as at the air-water interface, the MH^+ and M forms are in equilibrium.



The SHG efficiency of the Langmuir Blodgett (LB) films built with the cited compound must depend on the transferred form onto the substrate. Moreover the derived methyl compound exhibits a cis-trans isomerization which can be induced photochemically. Such an isomerization, may occur in the derived LB material which could become an information storage.

Compression isotherms of pure merocyanine spread on a ultrapure water surface exhibit a plateau at 16mN/m. The detectable surface pressure at large molecular surface areas may indicate a flat orientation of the polar heads at the air-water interface. A change in the structural monolayer must occur at 16mN/m, the head groups are probably lifted. The transfer of the monolayer onto hydrophilic fluorine substrates is of the Z type for all surface pressures.

The UV-visible spectra of M in $CHCl_3$ solutions present at 400nm the MH^+ absorption band. At 606nm we detect the M form and the shoulders at 576 and 540nm correspond to H aggregates. The absorption spectrum of LB films transferred at 25mN/m surface pressure, shows the MH^+ absorption band and a small shoulder at 500nm. Furthermore after few days we observed a vanishing of the shoulder and an increasing of the 400nm band. In our experimental conditions the mainly transferred form is the protonated.

Infrared studies of LB films and M, MH^+ in KBr matrixes have been made. The lack of the $1644cm^{-1}$ $>C=O$ absorption peak in LB material and in the MH^+ form confirms the UV-visible results. Furthermore the double pic at $1469cm^{-1}$ due to the alkyl chains indicates a tail group organization nearly perpendicular to the substrate.

Ammonia vapor reacts on the merocyanine LB films. At low pressures a new absorption band appears at 475nm which could indicate the formation of the M form. At higher pressures a continuous 1100-300nm absorption band appears and the films become more diffusive. When the ammonia vapor is removed the initial spectrum is found again. Ammonia vapor must reversibly change the form of the compound and the structure of LB films. Irradiations with a high pressure mercury lamp deteriorate the films.

LANGMUIR-BLODGETT FILMS OF POLYSILOXANES FUNCTIONALISED FOR NON-LINEAR OPTICAL APPLICATIONS

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Previous work has shown that certain polymers¹ form LB films with comparatively low scattering losses, and also that polysiloxanes² can exhibit second harmonic generation (SHG) in monolayer form. The present work is a study of LB films of polysiloxanes with the aim of obtaining a material with high SHG coefficient and low waveguide losses.

A variety of functional side groups based on azo dyes have been attached to polysiloxane chains of about 12 repeat units length with about 40% active side-groups, typically incorporating (CH₂)₆ spacer groups to increase flexibility. The previously-reported material with CH₂CH₂OH hydrophilic end-groups was found to produce exceptionally clear films; waveguide loss measurements are being undertaken. Contrary to previous reports this material, which does not have a specific acceptor group, did not show SHG when deposited from a pure water subphase. SHG was observed following depositing from an acid subphase, presumably due to protonation of the azo group. The efficiency was, however, only about 3% of that of hemicyanine.

Several other chromophores have been studied, and the strength of the SHG was found to increase with that of the acceptor group; further materials are under development. Not all the materials deposit well.

Other work has included the study of mesophases, and a correlation is being sought between the observed phases and, for example, the clarity of the deposited LB film. If it proves possible to maintain the high clarity of the original material whilst achieving high SHG efficiency, these materials could have practical significance. To that end, an alternating-layer trough has been fabricated for deposition of thick non-centrosymmetric films.

References

- [1] W.Hickel, G.Appel, D.Lupo, W.Prass and U.S.Cheunemann, *Thin Solid Films*, **210/211**, 182-4.
- [2] N Carr, M J Goodwin, A McRoberts, G W Gray, R Marsden, R M Scrowston, 1987: *Makromol. Chem., Rapid Comm.*, **8**, 487.

Thick Polymeric Langmuir-Blodgett Films for Efficient Second Harmonic Generation

by

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Non-centrosymmetric thick LB films of certain dye molecules exhibiting non-linear properties are of great interest in optoelectronic devices.

LB films prepared from non-polymeric amphiphiles are mechanically fragile and prone to reorganisation. This prompted us to study polymer films. These are certainly much less fragile and probably less prone to reorganisation.

Alternating all-polymeric LB films were built up using a fully automated double Langmuir trough. These films conformed to the theoretically predicted quadratic dependence of second harmonic generation for up to 150 bilayers. The effects of different degrees of substitution of the chromophore units and also the effect of using different polymers as the passive layers were studied. X-ray diffraction and ellipsometry studies confirm the uniformity of the films.

POSTERS

SESSION H: OPTICAL PROPERTIES & CHARACTERIZATION

PHOTOINDUCED CHARGE TRANSFER IN RHODAMINE B/ANTHRACENE
MIXED LB MULTILAYERS

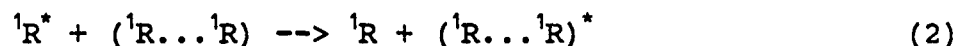
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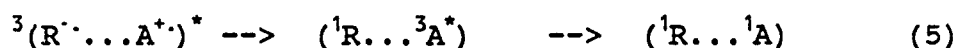
The photoexcited transient states of octadecyl rhodamine B (R) and 2-(9-anthroyloxy)stearic acid (A) mixed in a stearic acid (ST) matrix have been studied by flash photolysis and picosecond fluorescence methods in Langmuir-Blodgett (LB) films.

The R molecules in LB films exist predominantly as fluorescent monomers or nonfluorescent dimers. In the presence of A a ground state interaction between R and A molecules takes place. The interaction between R molecules in adjacent layers decreases the distance between monomers and makes the dimer formation between the layers possible.

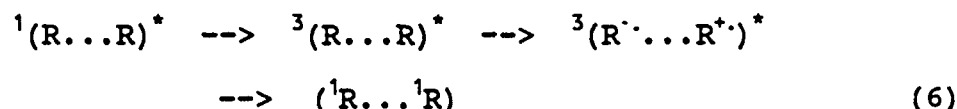
In the present films the dominant relaxation pathways in monomer sites are energy migration to lower energy sites and finally to dimers (processes 1 and 2), direct energy transfer to dimers (process 2), and charge transfer from A to $^1R^*$ (process 3)



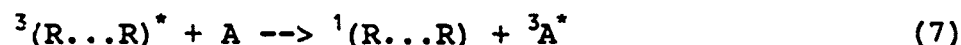
The lifetime of the electron-hole pair is so long that the triplet of R and A formed via processes 4 and 5 cannot be detected with the present measuring system



The absorption of the triplet of R observed in the transient spectra is formed via the relaxation of excited dimers (process 6)



The presence of R dimers and A together decreases the efficiencies of the charge transfer reactions (processes 3 and 4) via the triplet energy transfer from the triplet of the R dimer to A (process 7)



DETERMINATION OF LATERAL DIFFUSION COEFFICIENTS
IN AIR-WATER MONOLAYERS BY FLUORESCENCE
QUENCHING MEASUREMENTS

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Two-dimensional diffusion has been investigated in the phospholipid matrix dioleoyl-L- α -phosphatidylcholine (DOPC) at the air-water interface by studying the fluorescence quenching of a lipoidal pyrene derivative by two amphiphilic quenchers. The results have been analyzed in the theoretical framework of diffusion-controlled quenching in a two-dimensional environment to yield the mutual lateral diffusion coefficients.

Both steady-state and time-resolved techniques were employed and yield data which shows clear evidence for the features predicted for diffusion-controlled reactions in two dimensions. Analysis of the steady-state quenching behaviour as a function of quencher concentration produced non-linear Stern-Volmer plots. The time-resolved measurements yielded a single exponential lifetime for the pyrene chromophore in the absence of quencher, providing evidence that it is not aggregated in the monolayer film. In the presence of quencher the decays were non-exponential.

The lateral diffusion coefficients were found to be of the order of $10^{-7} \text{ cm}^2 \text{ s}^{-1}$. These values are comparable to those obtained in monolayer studies using the fluorescence recovery after photobleaching technique (FRAP), and approach in magnitude those reported for lipid bilayers and natural membranes.

The lateral diffusion coefficients were found to decrease with increasing surface pressure. This result reflects an expected decrease of monolayer fluidity when it is compressed.

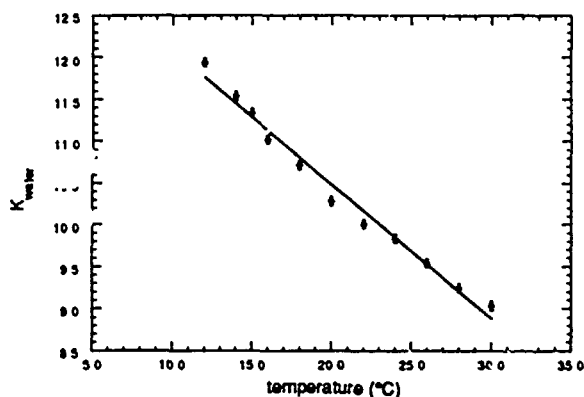
Optical Surface Heterogeneities Measured by Ellipsometry: Fatty Acid and Lipid Langmuir Monolayers at the Air/Water Interface

Michaela Paudler and Hans Riegler

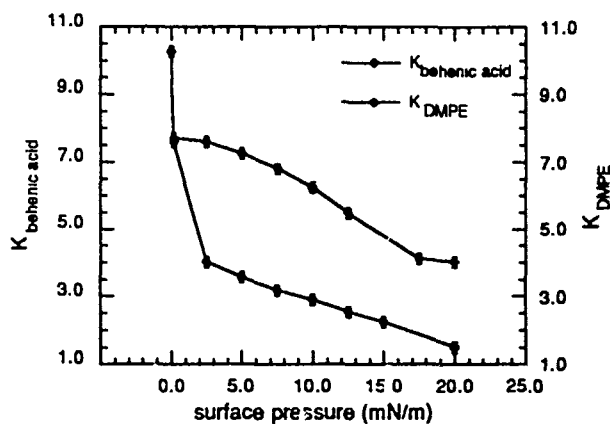
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Monolayers of fatty acids and lipids at the air/water interface are investigated via null ellipsometry in a series of systematic studies emphasizing on the shape of the intensity minima. The curvature K of the intensity minima seems to be related to the surface texture and may be a measure of the (generalized) optical surface roughness on a micron scale. The measured intensity signals and thus the curvature seems to be modified by the coherent interference of light reflected from interfaces with geometrical (e.g.

monolayer thickness) and/or optical (variations in the anisotropy) heterogeneities. This intensity modification seems to result in a decreased curvature K if the surface gets rougher, as can be shown by the measurement of K of a pure water surface as function of the temperature. K depends on the composition of the monolayer, the applied surface pressure, and the angle of incidence. Significant differences between fatty acid and lipid monolayers are observed.



Curvature K of the intensity minimum as function of the temperature for a pure water surface. The intensities were measured as function of the polarizer angle in a null ellipsometer setup. The analyzer angle and the angle of incidence were kept constant.



Curvature K of the intensity minimum of a behenic acid and a DMPE monolayer as function of the surface pressure. The intensities were measured as function of the polarizer angle in a null ellipsometer setup. The analyzer angle and the angle of incidence were kept constant.

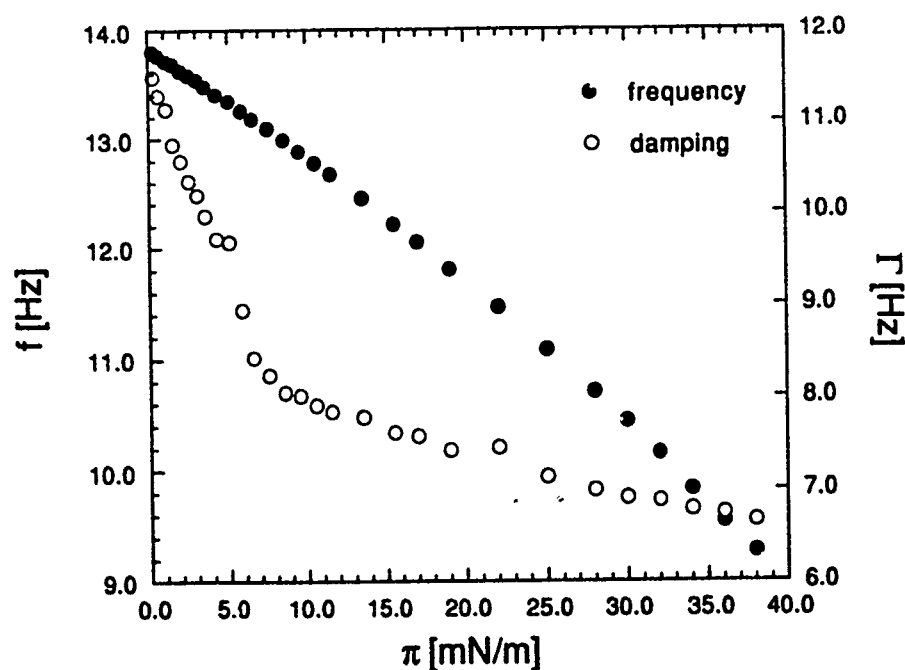
On the Correlation Between Viscoelastic and Structural Properties of Langmuir Monolayers
at the Air/Water Interface. Ellipsometric and Surface Light Scattering Studies.

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Langmuir monolayers of fatty acids and lipids at the air/water interface are investigated by surface light scattering (photon correlation spectroscopy) from thermally excited capillary waves. Thus information on viscoelastic monolayer parameters can be obtained. The object of our investigations is the relation between structural properties (derived from ellipsometry and x-ray diffraction) and dynamical properties as derived from surface light scattering.



Surface light scattering data for a DMPE monolayer ($T=20^\circ\text{C}$, $\Theta=64^\circ$, $q=487.9\text{ cm}^{-1}$).

**On The Study of the Morphology of the Langmuir-Blodgett Films Of Long chain
dynoic acid using FT-IR and Raman Imaging Techniques**

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The domain structure of the LB films of polymerised 10,12 pentacosadynoic acid has been studied using Raman imaging and FT-IR techniques with a view to monitoring and increasing the size of the domains of the LB monolayers of the PDA. Following a process of pre-annealing the Langmuir film by allowing the domains to relax on the water subphase through different length of times prior to transferring the film onto solid substrates, the grain size has been observed to increase from a few microns to around 30 microns while looking at the Raman image at the double vibration in the blue phase. The progress of the polymer growth within the domains was also observed. The influence of the spreading solvents has also been investigated. FT-IR measurements on monolayers deposited on an ATR crystal showed the evolution of the order of the PDA chains from the unpolymerised state through the initial "blue" phase to the final red phase state.

Preparation and optical characterisation of porphyrin derivatives as Langmuir and LB films.

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Several tetraphenylporphyrin (TPP) derivatives have been characterised as both floating Langmuir layers (on a range of different subphases) and as transferred LB layers. In particular, their optical absorption spectra have been recorded during monolayer compression. The peak absorption wavelength of such Langmuir layers have been compared with those from the LB layers and the spreading solutions. Surface pressure - area isotherms have aided our interpretation of the orientation of the molecules within the mono- and multilayer films.

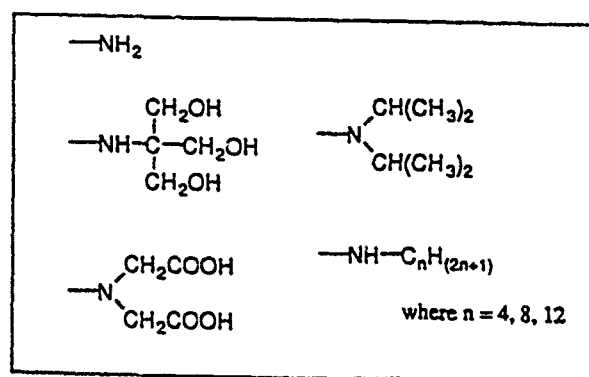
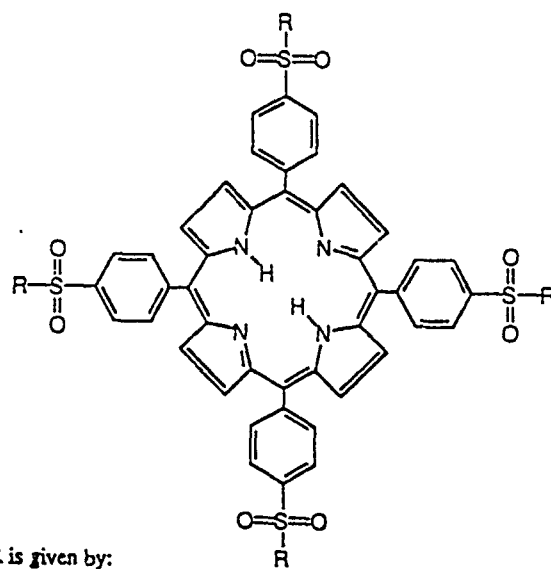


Figure 1 TPP Derivatives

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